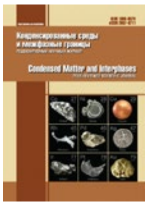

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Anomalous electron channeling in PZT thin films

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Abstract

The study of the surface of lead zirconate-titanate (PZT) thin films using a scanning electron microscope (SEM) identified the patterns of electron channeling on the surface of the perovskite phase crystals. However, the observation conditions were completely uncommon and contradicted model representations. Thus, there was enough evidence to believe that the observed patterns of electron channeling were an anomaly. It was necessary to conduct an additional detailed study of the perovskite crystal in a PZT thin film in order to clarify which conditions could cause this anomaly.

In particular, the method of electron backscatter diffraction (EBSD) in SEM was used to study the crystallographic specific features of the crystal. The method is based on the collection and automatic processing of electron diffraction patterns which calculate a corresponding crystallographic orientation for each point on the scanned crystal surface.

As a result, the study revealed the unusual features of the crystallographic structure of perovskite in a PZT thin film that provided an opportunity for the manifestation of anomalous electron channeling. The research showed that the crystal lattice of perovskite experienced an axially symmetric monotone bend, which determined the round shape of the crystal. The study demonstrated the possibility of producing ferroelectric crystals with a curved crystallographic surface. In order to describe the growth of round perovskite crystals from the amorphous phase in PZT thin films, the author provided a dislocation model where the continuous bending of the perovskite crystal lattice could be explained by the accommodation of mechanical stresses with a decrease in the phase volume of the film material. In addition, it was shown that the bands observed in the electron channeling patterns corresponded to crystallographic planes, while any distortions of the pattern indicated a local deformation of the lattice in a highly symmetrical uniformly curved perovskite crystal in a PZT thin film.

Keywords: Anomalous electron channeling, Channeling, Thin films, Lead zirconate-titanate, PZT, Perovskite, Deformed crystals, EBSD

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1. Introduction

The solid solutions of lead zirconate titanate (PZT) are among the main ferroelectric materials with properties suitable for IR detectors, microwave electronics, micro-electromechanical devices, and static and dynamic memory elements [1–6].

Electronic devices are being constantly improved, which also involves the development of radioelectronic components towards energy efficiency and smaller sizes. Thus, miniature, film, and thin-film versions of ferroelectrics are becoming increasingly widespread. However, it is known that with the decrease of film thickness, it becomes difficult to control the electrical characteristics of PZT films [7]. This trend is usually associated with the introduction of additional factors with an increasing impact of the surface. The final properties of the ferroelectric film are also more and more influenced by the characteristics of the substrate, such as the linear expansion coefficient, oxidation resistance, and barrier properties. Therefore, the task of studying thin-film ferroelectrics based on PZT appears to be highly relevant.

As for the research regarding PZT thin films, continuous perovskite films and films with an island structure are both essential. The term «island» here describes the round-shaped crystals that are formed during the annealing of PZT thin films. With a small concentration of crystallization centers, single islands of the perovskite phase in the amorphous matrix grow in the form of flat round-shaped crystals. As the number of the island crystallization centers increases, perovskite phases merge and form together a continuous surface [8–10].

The radiant patterns observed on the surface of the islands (Fig. 1) were also described in a number of works that present some assumptions about their nature [9–13].

This study analyses the structure of perovskite islands of PZT thin films grown on a Pt-TiO_2-sitall substrate. And the results of the study are presented in this article. Even at the stage of obtaining electron images (Fig. 2) from a scanning electron microscope (SEM), the islands looked different from what was observed in PZT films on Pt-TiO_2-SiO_2-Si substrates (Fig. 1). Thus, a pattern in the form of intersecting bands, similar to the Kikuchi diffraction pattern, could be seen in the electron image of a PZT film island on a sitall substrate (Fig. 2), instead of radially divergent radiant patterns. Electron images in Figs. 1 and 2 were obtained with normal incidence of an electron beam with an energy of 12 keV.

Similar patterns in SEM were observed in the case of bulk single crystals with significantly different angles of incidence of the scanning electron beam on the sample due to the manifestation of the electron channeling effect [14]. An example of the electron channeling pattern on a large-sized ingot of alpha-titanium alloy is presented in Fig. 3. The pattern was obtained from the most available field and was limited by the circle of the lens aperture. The

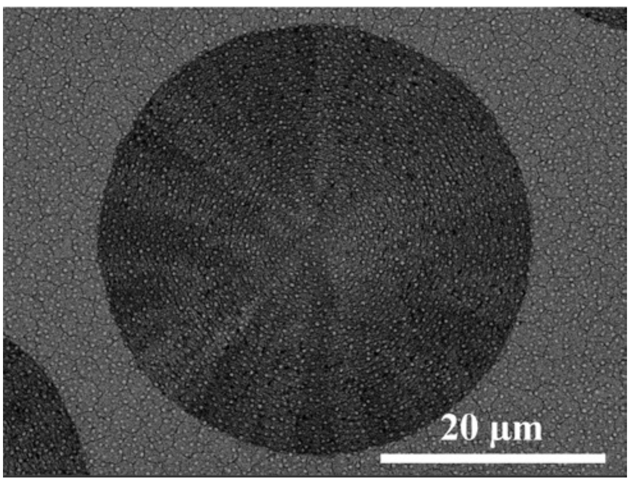


Fig. 1. The electron image of an island of perovskite in a thin film of PZT on a substrate Pt-TiO_2-SiO_2-Si

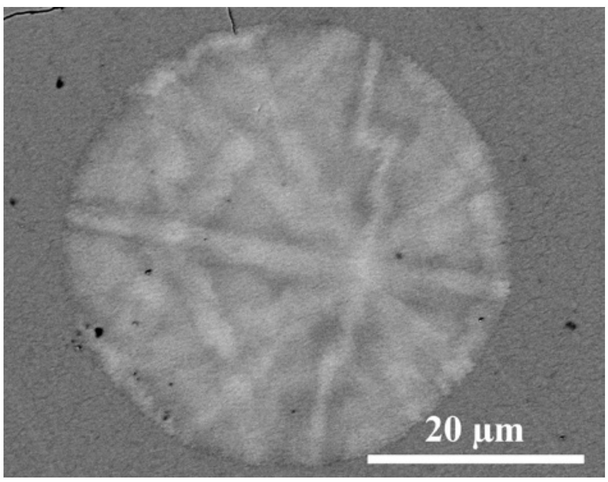


Fig. 2. The electron image of an perovskite island in a thin film of PZT on a substrate Pt-TiO_2-sitall

difference in the angles of incidence of the electron beam on the crystal surface aimed at obtaining the pattern shown in Fig. 3 was 30°.

The channeling of charged particles in crystals could be explained by the movement of particles along the "channels" formed by parallel rows of atoms (Fig. 4a). In this case, the particles experience sliding collisions (the momentum did not change significantly) with rows of atoms that hold them in these "channels." If the particle path is between two atomic planes, this can be called planar channeling [15, 16]. During beam incidence on a crystal lattice at significantly different angles (Fig. 4b), it encounters planes with low atomic density on its way, along which electrons channel before scattering [16, 17].

As you can see, if the scale markers in Figs. 2 and 3 are compared, the observing conditions for electron channeling patterns on perovskite islands differ from those described above. The perovskite island is small and is scanned with a very small discrepancy by almost parallel electron beams (the angle of the electron beam deflection did not exceed 0.15° while scanning the island along its diameter). The effect upon which the channeling pattern was observed when irradiated by parallel beams was an anomaly that contradicted model representations. Thus, the electron channeling effect observed on perovskite islands in PZT thin films prepared on a Pt-TiO_2-sitall substrate was an anomaly.

The goal of this work was to study the structural features of perovskite islands that formed the conditions for observing anomalous electron channeling in a thin layer of PZT films.

2. Experimental

A PZT thin film in which the effect of anomalous electron channeling was observed, was deposited on a layered substrate. The layered substrate was a system of textured platinum (with the crystallographic plane (111) egressing to the surface) with a thickness of about 0.2 μm which was deposited on a titanium dioxide sublayer (about 20 nm) located on a thick (approximately 0.5 mm) ST-50 sitall substrate. The films were deposited using high-frequency magnetron sputtering of a PZT ceramic target with a composition corresponding to the morphotropic phase boundary. Upon deposition, the amorphous films were annealed in an oven in order to crystallize the perovskite phase in them. Heated at a rate of 300 °C/hour up to 570 °C and kept for 1 hour, the films as well as the oven were cooled to room temperature.

Such widespread research techniques as optical, scanning electron, and atomic force microscopy do not provide information about the crystallographic specific features of the material when they are used to analyze film structures [18]. However, electron backscatter diffraction (EBSD), which combines the possibility to analyze

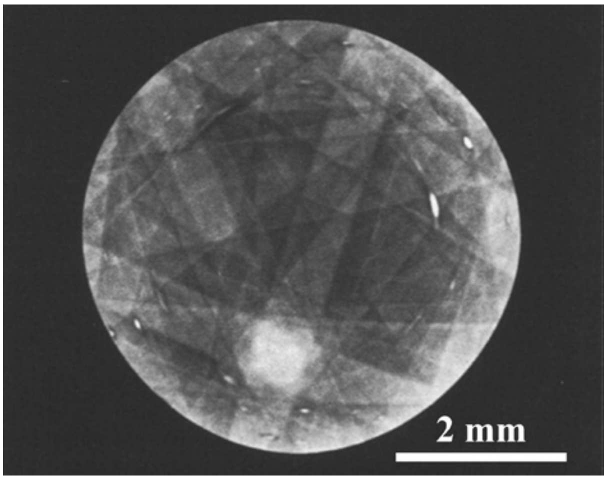
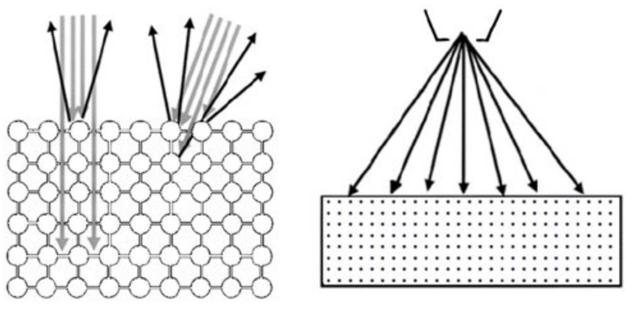


Fig. 3. An example of an electron channeling pattern obtained on a large-sized alpha-titanium alloy ingot. The observation of the picture is limited by the objective aperture of the SEM. The scale marker makes it possible to evaluate the characteristic conditions for observing the pattern of electron channeling



a b

Fig. 4. A schematic diagram showing the origin of the channeling effect as the penetration of beam electrons along the crystal planes (a). Scanning at low magnification of the SEM is associated with a significant change in the incidence angeles of electrons on the crystal surface (b)

local crystal orientations and SEM high spatial resolution, is a suitable method for studying the features of crystalline phases in thin films.

Thus, the PZT films annealed in the oven were studied using a Tescan Lyra 3 scanning electron microscope (SEM) equipped with a system for recording EBSD patterns. The EBSD method involves point scanning of a sample and also registering and processing the resulting electron diffraction patterns. The lack of accuracy while determining crystal orientations regarding the macroscopic SEM-related coordinate system using EBSD (error 1–2°) did not affect the angular resolution when analyzing relative orientations between two close points [19]. Crystallographic orientation maps accumulated using the EBSD method can clarify the origin and nature of the structural features of crystals and help to explain the mechanisms of their growth.

During the study, it was experimentally confirmed that a change in the electron beam parameters while scanning the studied surface did not result in physical degradation or phase transformations on the surface of a PZT thin film. Therefore, the accelerating voltage and the beam current were selected in accordance with the achievement of a suitable mapping speed with sufficient resolution of the Kikuchi diffraction patterns and their exposure. The scanning step and digital resolution of the accumulated map were determined using the representativeness of the display of the relevant structural features at a certain SEM magnification. The obtained diffraction patterns were indexed taking into account the relative position of 10–12 Kikuchi bands in order to avoid the "pseudosymmetry" issues, which led to incorrect conclusions in [20]. In a series of trial studies, similar to [20], data on tetragonal, monoclinic, and rhombohedral crystal lattices typical for PZT were entered into a computer program so as to analyze the diffraction patterns. However, as the results showed, the lattice parameters and angles (with a deviation of no more than 0.4°) were so similar that it was impossible to distinguish them using this method. Therefore, in order to describe a real crystallographic system, it was decided to use deformed pseudocubic lattice approximation.

3. Results and discussion

The map of crystallographic orientations of a perovskite island accumulated using EBSD in a PZT thin film on a Pt(111)-TiO_2-sitall substrate is shown in Fig. 5 on the left. The lattice orientation in each map point is encoded using a standard inverse pole figure (IPF) color distribution built for the macroscopic direction that coincides with the surface normal to the sample surface plane. The color coding IPF for a pseudocubic perovskite

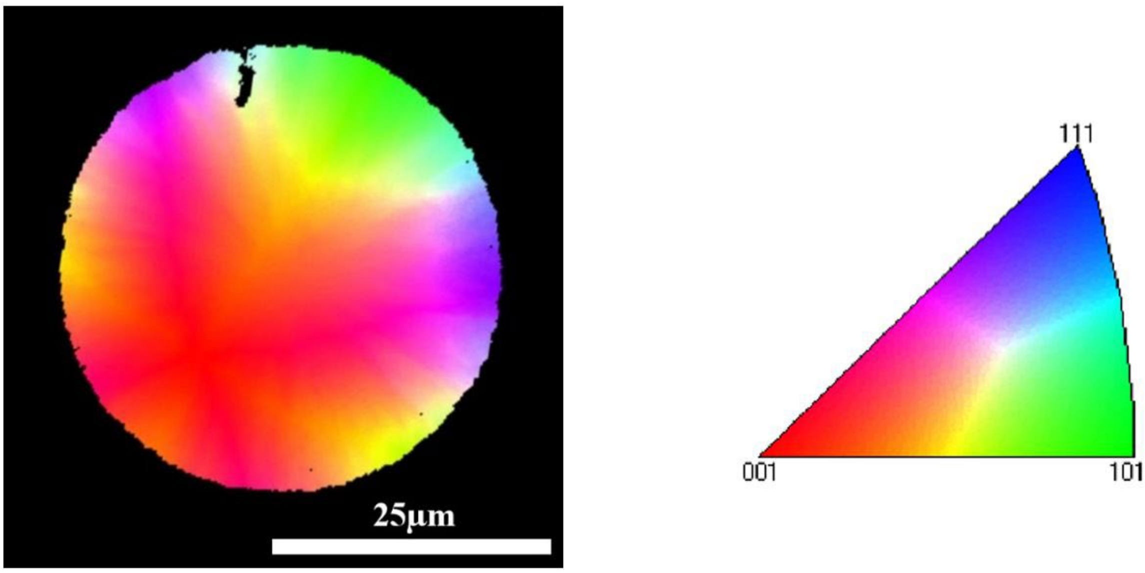


Fig. 5. A map of the crystallographic orientations of the perovskite crystal and a color coding triangle for it

lattice is presented in Fig. 5 on the right. The areas marked in black on the map of crystallographic orientations are those where scanning obtained Kikuchi diffraction patterns that were not suitable for processing.

As it can be seen, the island structure is encoded with smoothly spread color gradients, with no expressed crushing into radially divergent "rays" that are typical for perovskite islands in PZT thin films on Pt(111)-TiO_2-SiO_2-Si [9].

The software for processing orientation maps allowed information to be obtained about the crystallographic disorientations achieved within the studied island. Therefore, based on the orientation map (Fig. 5), maps of grain reference orientation deviation (GROD) from a certain average orientation calculated for a specific island (Fig. 6) were plotted. The deviation angles of the crystal lattice orientations in each point on the GROD map are encoded in the colors of the map key.

The resulting GROD map (Fig. 6) indicates the presence of a homogeneous axially symmetric deformation of the crystal lattice of the perovskite phase island. It can be clearly seen that the crystal lattice of the island was evenly deformed in all radial directions in relation to the center of the island, the orientation of which obviously coincided with the growth nucleus. The profile of changes in crystallographic orientation angles calculated along the radial directions (Fig. 7) indicates the linear and monotonously continuous nature of the lattice rotation from the starting to the ending point. The lattice rotation gradient calculated from the profile was 1.4 °/μm.

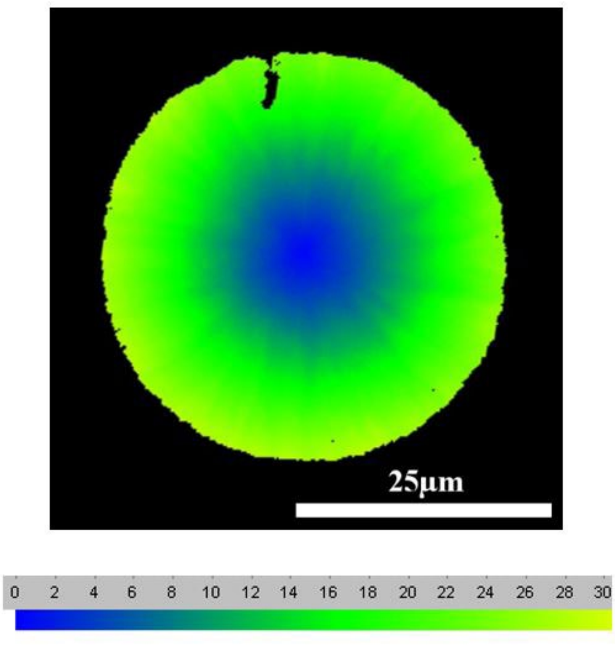


Fig. 6. GROD – a map of the perovskite island and the colour legend for it

Taking into account the identified homogeneity of the crystal lattice rotation in all possible radial directions (Figs. 5–7), it is reasonable to interpret the effect observed in Fig. 2 as an electron-optical anomaly associated with the specific features of the crystallographic structure of perovskite islands in a PZT thin film grown on a platinized sitall substrate. The anomalous effect of electron channeling appeared due to a homogeneous axially symmetric distortion of the crystal lattice of the island. Due to the monotonous and continuous bending of crystallographic planes represented by the model in Fig. 8 [21], the angles of electron entry into the crystal lattice also changed, and it was possible to observe the pattern of electron channeling in parallel electron beams.

What is more, the author noted that if the slope of the sample in the SEM chamber changed (for instance 10°) while observing the surface of the perovskite phase islands (Figs. 2, 9a) then the system of mutually intersecting lines on the island shifted (Fig. 9b). This shift could be explained by a change in the position of the crystallographic planes relative to the electron beam falling on them, i.e., the angle of electron entry into the crystal lattice.

It can be easily shown that the lines observed in the electron channeling patterns corresponded to crystallographic planes [14–17]. Therefore, the position of the crystallographic planes could be directly observed in Figs. 2 and 9. Any additional stresses applied to the film were expressed as a distortion of the electron channeling pattern. In particular, the "break" of the vertical line in Fig. 2 can indicate local deformations of the crystal lattice in a highly symmetric and homogenously curved perovskite crystal.

A dislocation model can be suggested to describe the growth of perovskite islands from the amorphous phase in a thin layer of a PZT film. The lattice rotation in this model occurs as a result of the accommodation of mechanical stresses

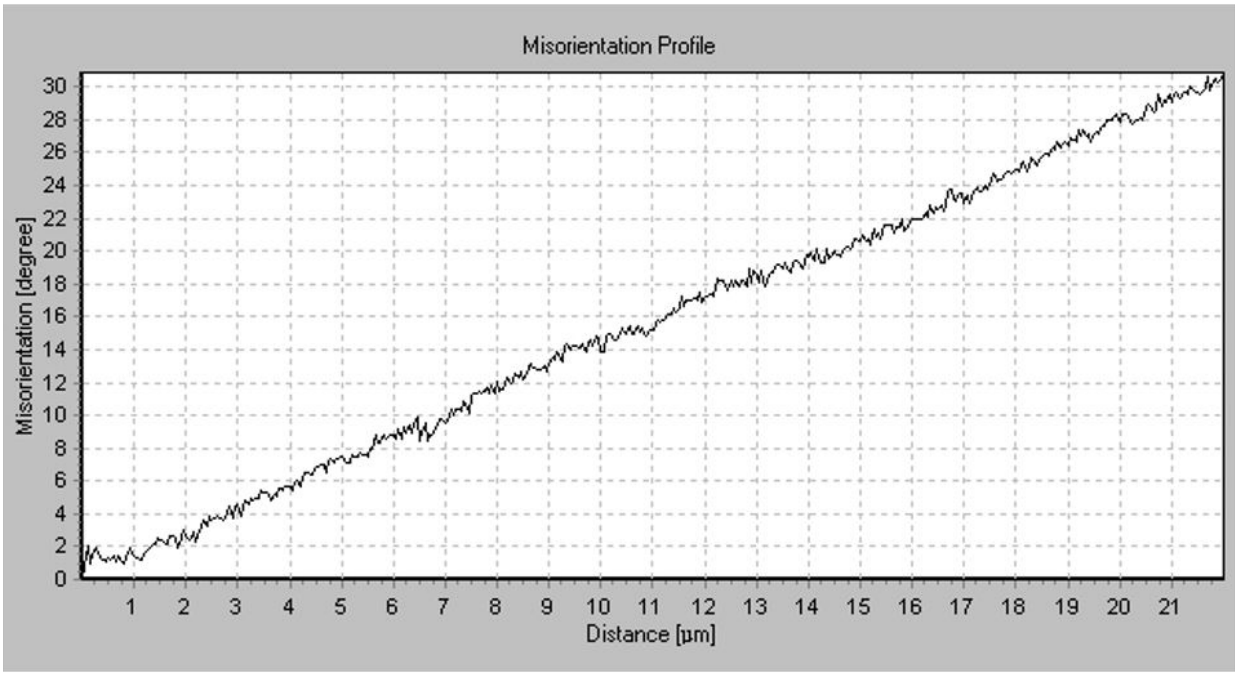


Fig. 7. The profile showing the change in the orientation angle of the crystal lattice of the perovskite island measured radially

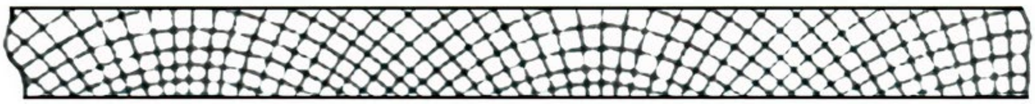
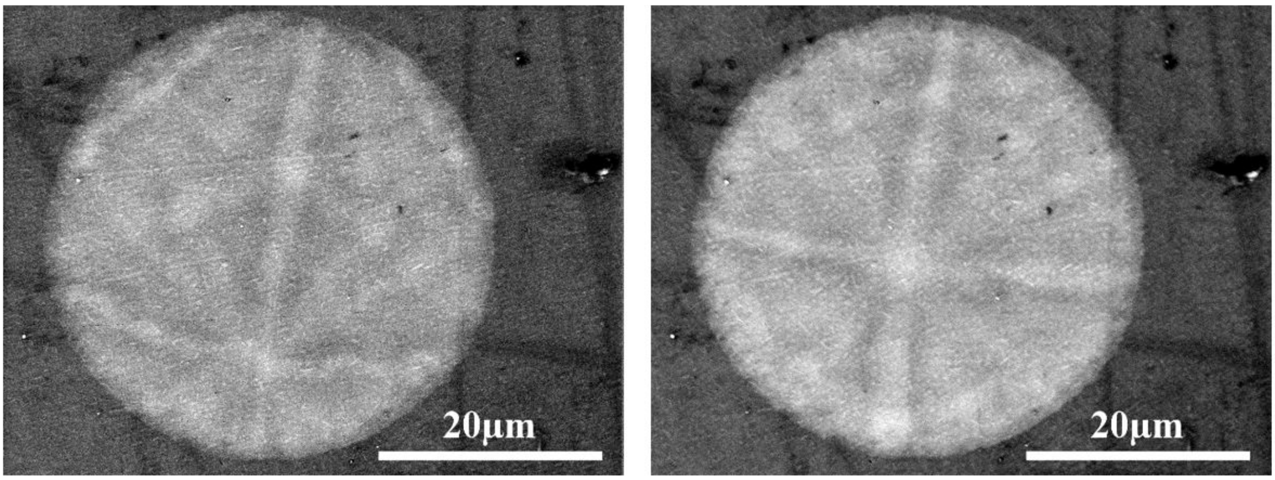


Fig. 8. An exaggerated model showing the bending of the crystal lattice planes



a b

Fig. 9. Electron images of the perovskite island showing a combination of intersecting stripes. In the image a) the incidence angle of the scanning electron beam in the center of the frame is close to normal. Image b) was received after physically rotating the sample around the horizontal axis by 10 degrees

upon a change in the phase volume. This model is adapted for PZT thin films of the model presented in [18, 22, 23]. The model contains assumptions that the crystallization front near the surface was ahead of the front near the substrate and that on the whole this front was propagating in a direction parallel to the film-substrate interface.

Thus, in the course of the crystallization, the material was considerably densified due to shrinkage along the pyrochlore-perovskite interface. For a thin film, in particular, the density increased perpendicular to the free surface, as only in this direction the change in shape was unlimited [22]. An additional half-plane appeared on the crystal side due to the smaller distance between atoms (of higher density) of the crystalline state. These unpaired dislocations, which initially appeared at the perovskite-pyrochlore interface, remained in the bulk of the growing crystal and formed a cloud of geometrically necessary dislocations responsible for the “bending” of the entire crystal lattice inside the crystal. This model is illustrated in Fig. 10 using a set of curved lattice planes that were initially parallel to the surface (left side of Fig. 10) and gradually bended towards the substrate with the growth of the crystal. According to the model, during island growth the lattice rotation axis should lie in the plane of the film, perpendicular to the direction of movement of the crystallization front. This position of the rotation axis with the constant rotation angle is a condition for the formation of the observed round-shaped crystals.

The suggested dislocation model can be experimentally verified by accessing the predicted density of dislocations. A relatively simple formula can be used for a theoretical evaluation of the local plane of dislocations in case of their homogenous distribution [24,25]:

$$\rho_{\text{hom}} = \frac{\theta_{\text{tot}}}{|b|\,\Delta X},$$

where θ_{tot} is the lattice bending angle at the distance ΔX implemented using dislocations with Burgers’ b vector.

Provided that $\theta_{\text{tot}} = 28^{\circ}$, $\Delta X = 20$ µm, and $|b|$, which equals to a pseudocubic lattice period ($a = 4.05$ Å), the average density of dislocations inside the perovskite island must take on a value of $3.5\cdot10^{15}$ m^{-2}.

4. Conclusions

A new phenomenon, an anomalous electron channeling, was discovered in PZT thin films on a sitall substrate. It was possible to observe the channeling patterns on the surface of perovskite islands upon radiation with parallel electron beams due to their unusual crystallographic structure. Based on the example of an individual

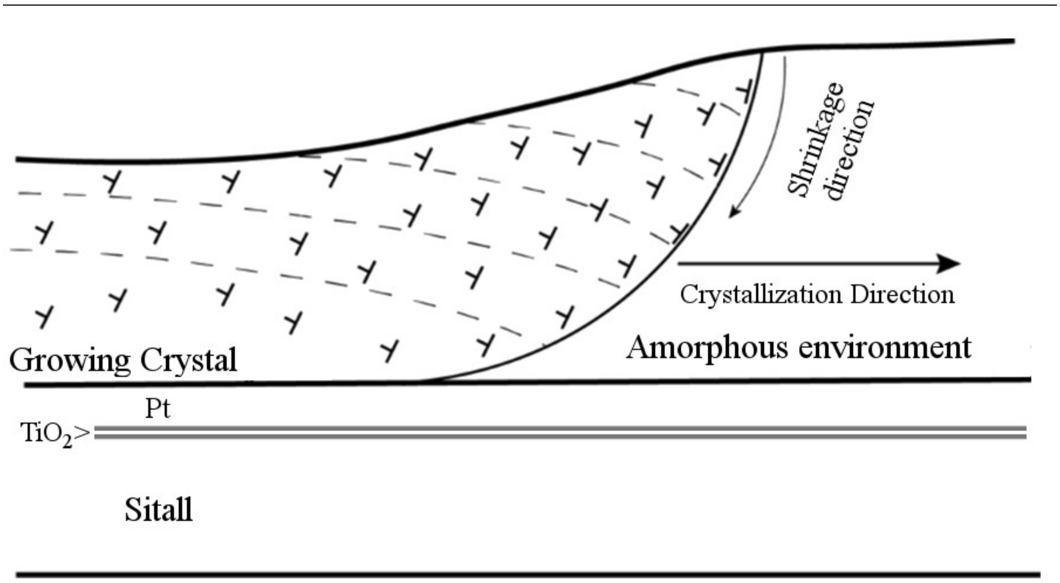


Fig. 10. An illustration of the dislocation model showing the bending of a perovskite island crystal lattice while growing from a quasi-amorphous environment

island, it was established that the crystallographic lattice of the islands had an axially symmetric bend increasing with the distance from the center according to the linear law. Therefore, it was shown that crystals with a symmetrically curved crystallographic surface could be obtained in thin films. A verifiable dislocation growth model was suggested for perovskite islands with a curved crystallographic surface from a quasi-amorphous surrounding in thin PZT thin films.

Contribution of the authors

The authors contributed equally to this article.

Conflict of interests

The authors declare that they have no actual or potential competing financial interests or personal relationships that could have influenced the work reported in this paper.

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