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Deformation of the crystal lattice during the formation of a spherulite microstructure in thin films of lead zirconate

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The reversal of the crystal lattice during the formation of spherulite islands in thin films of lead zirconate-titanate is studied using scanning electron microscopy by diffraction of reflected electrons. It is shown that the lattice reversal in spherulites can occur both towards the center of the spherulite and towards its periphery. The mechanisms of formation and growth of spherulites are considered to explain the observed effect.

Keywords: thin films of lead zirconate, CTS, rotational crystals, spherulite microstructure, reversal mechanisms.

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1. Introduction

A spherulite microstructure is formed in thin films of lead zirconate-titanate (LZT) in process of high-temperature annealing of amorphous layers previously deposited on a cold substrate. This process may involve both physical (vacuum) deposition methods [1–3] (such as ion-plasma sputtering or laser ablation), and chemical methods (sol-gel, CVD, MOCVD) [4,5]. In process of film annealing the perovskite phase crystallization happens by formation and growth of perovskite islands from the intermediate low-temperature pyrochlore phase. Since a perovskite (Pe) lattice is more densely packed compared to a pyrochlore (Py) lattice, phase Py–Pe transformation is accompanied with appearance of strong stretching mechanical stresses (σ) in the plane of the film acting at the perovskite island from the side of the pyrochlore matrix, Figure 1. This causes deformation of a perovskite lattice that consists in rotation of a growth axis to form edge dislocations [6,7]. Previously such rotations (bends or curves) of the lattices were observed in thin films of various materials, for example, in antimony sulfide (Sb_2S_3) [8], quartzes (SiO_2 , GeO_2) [9–11], hematite ($\alpha\text{-Fe}_2\text{O}_3$) [12], indium oxide (In_2O_3) with addition of silicon (InSiO-films) [13] and in a wide range of other metal oxides, semiconductor alloys (Cd–Te, Ge–Te, Ti–Se) [14] etc. Such crystalline formations are related to a type of so called rotational (or transrotational) crystals [8–15]. According to [12,14], the bend of the crystalline lattice is of elastic nature, however, in later studies [7–11]

it is suggested that the lattice rotation is accompanied with appearance of edge dislocations, which, evidently, partially relaxes mechanical stresses. Even though, according to the ideas on the edge dislocations, their appearance is not at all always accompanied with rotation of a crystalline lattice [8,16].

Papers [8–10,13] found that the vector of the growth axis rotation in the crystalline lattice in the thin film is

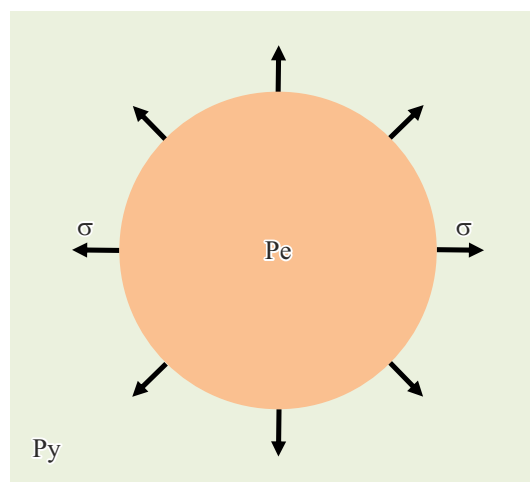


Figure 1. Schematic image of the action of lateral mechanical stresses at a perovskite (Pe) island from the side of a pyrochlore (Py) matrix.

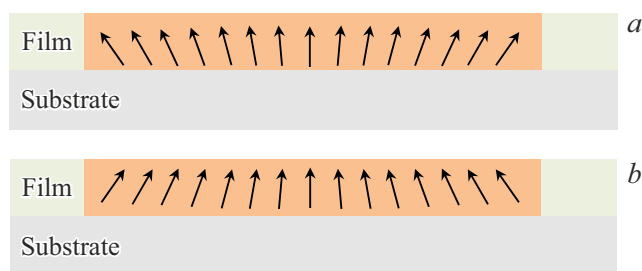


Figure 2. The observed rotations of the growth axis (crystalline lattice) in spherulite thin films: *a*) from the center to periphery of the island, *b*) from the periphery to the center of the island.

oriented from the center of the spherulite island towards its periphery, Figure 2, *a*. In particular, this conclusion is made by the authors of paper [13] based on reverse electron diffraction patterns and arrangement of straight pole figures in the thin film of indium oxide with addition of silicon (InSiO-film). On the opposite, it is assumed in the thin films of hematite and semiconductor alloys that the lattice rotates towards the center of the spherulite island [12,14]. Analysis of the literature dedicated to the study of rotational crystals demonstrated that until the present time the causes of a certain rotation have not been discussed in any way or studied substantively. Therefore, the objective of this paper was the experimental study of the lattice rotation nature in spherulite thin films of LZT, formed by variation of the process parameters of their manufacturing, and the detection of physical mechanisms that are responsible for these rotations.

2. Specimen preparation and study methods

LZT films were deposited on the platinized substrates of sitall CT-50 (Pt/TiO₂/sitall) and silicon (Pt/TiO₂/SiO₂/Si) by two-stage method of high-frequency magnetron sputtering. The composition of the sputtered ceramic target corresponded to the area of morphotropic phase boundary and met the elemental ratio of zirconium and titanium atoms Zr/Ti = 54/46. To produce the two-phase structure in the form of separate perovskite islands with diametral dimensions within 30–40 μm, surrounded by the matrix of low-temperature phase of pyrochlore, the deposited amorphous films were exposed to annealing at temperature of 530 °C on a sitall substrate and at 550 °C on a silicon substrate. The thickness of LZT films was 900 and 500 nm, accordingly.

The crystalline structure and phase state of films were measured by the X-ray diffraction analysis method (Rigaku Ultima IV). Microimages of spherulite islands were obtained using a scanning-electron microscope (Tescan Lyra 3), equipped with a detector to record the reflected electron diffraction patterns. Processing of diffraction patterns allowed us to generate point-by-point orientation maps of

spherulite islands with data on crystal-lattice orientations (pole figures), to construct maps of the distribution of disorientation angles within each island on their basis (GROD — grain reference orientation deviation), and to determine the speeds of crystalline lattice rotation.

3. Experimental results and discussion

Figure 3 presents the results of studying the diffraction patterns of reversely reflected electrons in two spherulite islands formed on the platinized sitall (Figure 3, *a, c, e, g*) and silicon substrates (Figure 3, *b, d, f, h*) as a result of high-temperature annealing of amorphous films and their crystallization from the matrix of intermediate low-temperature phase of pyrochlore. Despite the approximately same linear dimensions (around 40 μm in diameter) of perovskite islands, they were significantly different by microstructure and nature of crystalline lattice rotation. Orientation maps of the islands mean the following: in the first case (Figure 3, *a*) <100>-growth orientation of the island is close to the normal line to the surface, and steady change of the growth axis orientation is observed in accordance with the smooth change of the color gamma from the center to the periphery of the spherulite island; in the second case (Figure 3, *b*) <111>-growth orientation of the island is close to the normal line to the surface, and the island itself is characterized by the radial-fibrous microstructure and sharp change of color gamma in the adjacent raylets. GROD-maps of the islands demonstrated that if in the first island axially homogeneous rotation of the crystalline lattice takes place with the speed of ~ 1.4–1.5 deg/μm (Figure 3, *c, e*), then in the second island the speed of rotation changes from a raylet to a raylet, and its value turns out to be much lower and makes ~ 0.4–0.8 deg/μm (Figure 3, *d, f*).

The reasons for the axially homogeneous rotation in the first case are obviously related to low roughness of the platinum sublayer surface, which causes formation of perovskite crystallites (with size of 50–100 nm) with orientation correlation of grains in the film density. In this case the spherulite microstructure is formed by small-angle crystalline branching [13]. As the roughness of the platinum sublayer increases (in LZT/Pt/SiO₂/Si) the probability of orientation correlation of crystalline grains in the film plane decreases, and appearance of radial-fibrous structure reflects the mechanism of small-angle non-crystalline branching [13,17]. Decrease in the speed of lattice rotation in this case is related to appearance of radial boundaries and partial relaxation of lateral mechanical stresses in them.

Figure 3, *g, h* includes images of straight pole figures for orientation of type <100>, which may be used to decide on the rotation directions of the crystalline lattice. Analysis of the orientation maps and straight pole figures confirms that in the first case the lattice rotation happens from the center to the periphery (Figure 2, *a*), while in the second case the rotation happens quite on the contrary — towards the

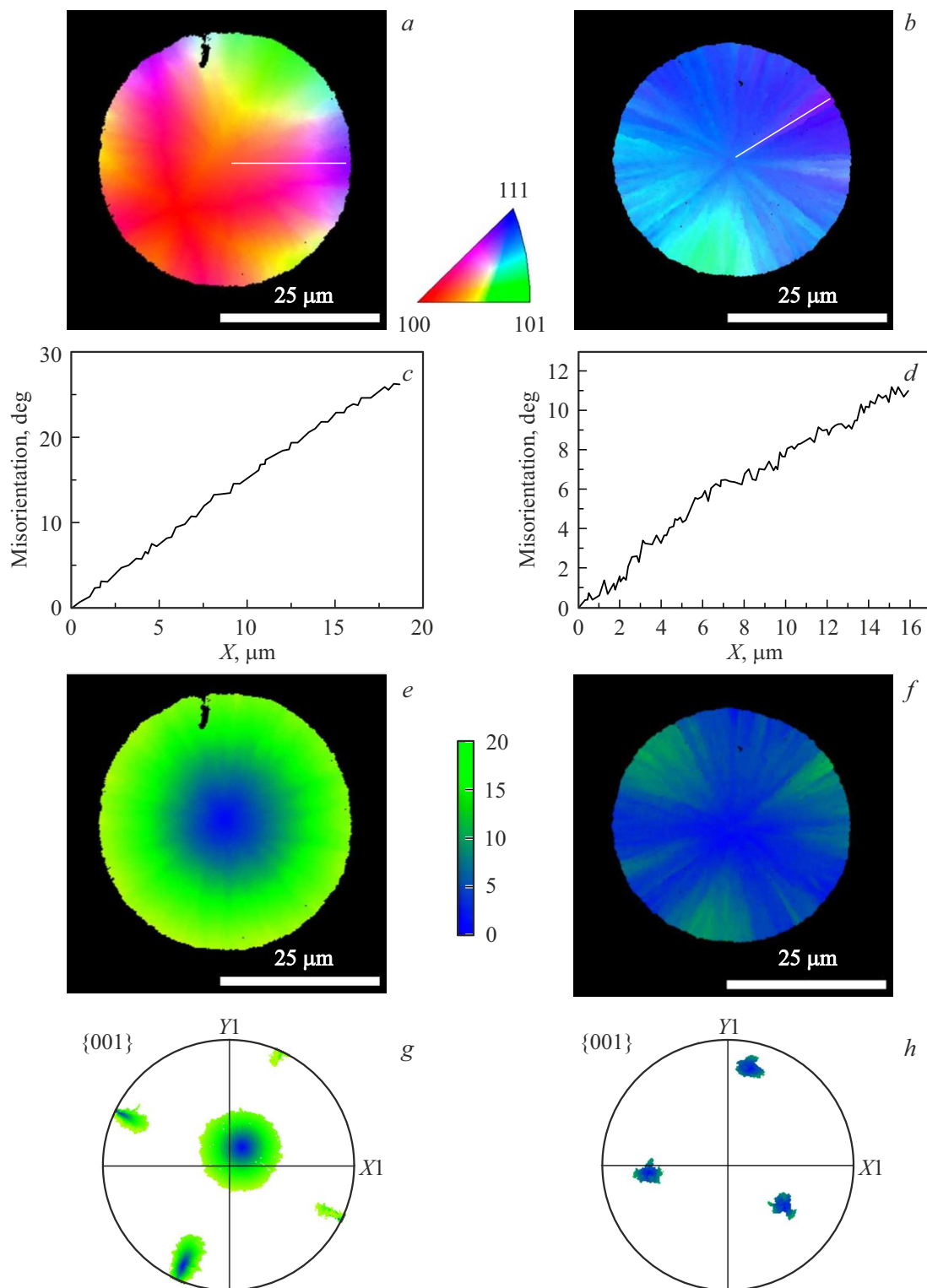


Figure 3. Diffraction (*a, b*) and GROD (*e, f*) maps, straight pole figures (*g, h*) and radial dependences of lattice rotation angles (*c, d*) in two spherulite islands, formed by annealing of amorphous thin LZT films formed on platinumized sital (*a, c, e, h*) and silicon (*b, d, g, h*) substrates.

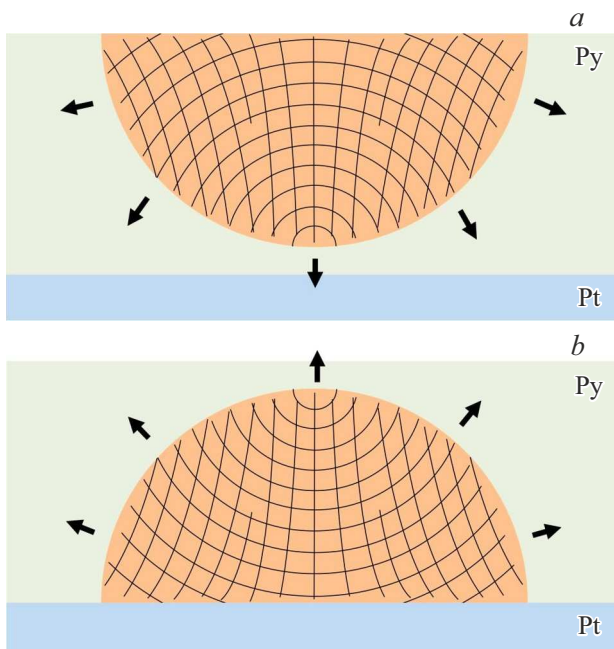


Figure 4. Schematic image of crystalline lattice rotation for different locations of origination and growth of perovskite (Pe) phase islands in the pyrochlore matrix of the thin film: *a*) from free surface, *b*) from the lower boundary of the film and the substrate (lower Pt electrode), *c*) in the film volume.

center of the island (Figure 2, *b*). Therefore, the provided results mean that the thin LZT films may implement the formation of spherulites that differ in the direction of the lattice rotation relative to the center.

To explain the observed effects, you may use a schematic image of the model reflecting the origination and growth of spherulite islands: *a*) at the upper boundary (near free surface) of the film (Figure 4, *a*) and *b*) at the lower interface (near the interface of the film and the lower electrode) of the film (Figure 4, *b*). Using this model, we have previously explained the changes in the physical properties and composition of thin LZT films in process of perovskite phase crystallization at the annealing temperature change.

According to the presented model, the growth of perovskite islands from the side of the free surface is accompanied with the appearance of elastic deformation by rotation of the lattice towards the direction of the spherulite center at stresses below the plastic limit, and at stresses above the plastic limit, plastic deformation is added to form edge dislocations. Similar mechanism of crystalline lattice rotation will take place when the spherulite originates and grows from the bottom interface. Besides, in the experiment, when the rotation is fixed by method of reflected electron diffraction, in the first case the lattice rotation is observed from the center of the island to its periphery (Figure 3, *a, g* and Figure 4, *a*), and in the second one — to the opposite side, towards the spherulite center

(Figure 3, *b, f* and Figure 4, *b*). Therefore, the direction of the crystalline lattice rotation may be used to decide on the features of origination and growth of the spherulite structure in thin films.

Estimates of the elastic strength value for thin LZT films made in paper [7] at room temperature are ~ 580 MPa, and the estimates of the maximum mechanical stresses made for the spherulite structures that we investigate, are comparable to the experimentally measured value and do not exceed ~ 500 MPa [18]. Therefore, it seems that in the presented model you can avoid involvement of edge dislocations. However, dislocations are formed not at room temperature, but at temperature of perovskite phase crystallization (above 500°C), where the value of the elastic strength may be lower by several orders than at room temperature. Therefore, the real structure for estimation of density of edge dislocations (ρ_d) usually applies formula [9]:

$$\rho_d = \varphi / (r \cdot |\mathbf{b}|), \quad (1)$$

where φ — lattice rotation angle, r — distance, at which the lattice rotation is determined, \mathbf{b} — Burgers vector. For the lattice rotation speed $v = \varphi/r = 1 \text{ deg}/\mu\text{m}$ and $|\mathbf{b}| = 0.4 \text{ nm}$ (value equal to the parameter of the perovskite lattice), the density of dislocations achieves $\sim 4.3 \cdot 10^{13} \text{ m}^{-2}$, which by the order of the value matches the values determined in quartz films [9]. At the same time the question of how the lattice is rotated — to form edge dislocations or via a more complicated mechanism called disclination, is still being disputed [8–12].

4. Conclusions

It was found that two types of crystalline lattice rotation were implemented in thin spherulite LZT films: from the center of the island to the periphery and from the periphery to the center of the island. It is assumed that the direction of the lattice rotation depends on the place of island origination and growth — from the upper surface of the thin film, from the interface with the substrate (lower electrode). It is entirely possible that a more complicated variant of origination and growth of the island in the volume of a thin film may be implemented [19].

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Conflict of interest

The authors declare that they have no conflict of interest.

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