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Change in the rotation speed of the crystal lattice in spherulitic thin films with increasing their thickness

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The thickness dependence of the lattice rotation rate (gradient) in submicron spherulitic films of lead zirconate titanate (PZT) was studied using the electron backscatter diffraction method. Analysis of the lattice rotation rate dependence on the thickness showed that a decrease in the PZT layer thickness leads to the appearance of plastic deformation; the mechanisms of its formation are discussed.

Keywords: spherulitic microstructure, lead zirconate titanate thin films, rotational crystals, electron backscatter diffraction.

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The interest in a wide variety of diverse compounds crystallizing from the amorphous phase through the nucleation and growth of islands with a shape close to spherical (in bulk materials) or to a flat cylinder (in thin films) has been on the rise lately. Such polycrystalline structures are called spherulites. The key distinguishing feature of their growth is the so-called low-angle non-crystalline branching [1,2]. The physical properties of these spherulitic structures have been little studied to date, and their application potential remains unclear.

Thin-film materials differing in composition and crystal structure (including polar materials in which axial-radial rotation of the crystal lattice from the center of spherulitic islands (blocks) to their periphery was observed [3–12]) are of particular interest. Specifically, the study of nanometer-thick films of hematite (α-Fe_2O_3) and lead zirconate titanate with added lanthanum (PLZT) revealed that the lattice rotation rate reaches enormously high values (100 deg/μm and more). As a result, such crystalline formations were called transrotational crystals [3–5]. However, since significantly smaller lattice rotations (from a fraction to several units of deg/μm) were observed in a number of subsequent studies of submicrometer spherulitic films, such structures were simply called rotational crystals [6–12].

The crystal lattice rotation in thin films is often attributed to the emergence of lateral mechanical stresses as a result of high-temperature annealing of previously deposited amorphous films, since the density of the crystalline phase is typically higher than the density of the amorphous phase (or intermediate low-temperature phase) [7,8]. This difference was 20 % in quartz and $\sim$ 8 % in PZT in the case of crystallization of the perovskite phase from the intermediate pyrochlore phase [7,11], which led to the emergence of strong tensile mechanical stresses in the substrate plane and bending deformation of the crystal lattice. The magnitude of mechanical stresses is potentially affected to a certain extent by the annealing temperature, the difference in temperature coefficients of linear expansion of the thin film and the substrate, the orienting effect of the substrate, and possible recrystallization of the thin film itself. Strong stretching of a thin layer may lead to the formation of pores and cracking [13]. This influence of tensile and bending mechanical stresses may lead to the reorientation of spontaneous polarization in directions as close as possible to the substrate (film) plane, to the formation of radially oriented self-polarization in thin PZT films, and to the directed diffusion of vacancies (charged ones included) in directions normal to the forces stretching the perovskite lattice [14–16].

The results of experimental studies of rotational crystals indicate that the lattice rotation rate (gradient) of a thin film increases as this film grows thinner. However, this thickness dependence of the rotation rate has not been investigated to date. The aim of the present study is to examine the above-mentioned dependence in submicrometer spherulitic PZT films, which have potential applications in microelectromechanical devices, by electron backscatter diffraction.

Thin spherulitic (polycrystalline) PZT films were prepared using a two-stage (*ex situ*) method of RF magnetron sputtering of a ceramic target with a composition corresponding to the region of the morphotropic phase boundary [11]. At the first stage, amorphous films were deposited onto platinized silicon substrates at a temperature of 140 °C. At the second stage, these films were annealed

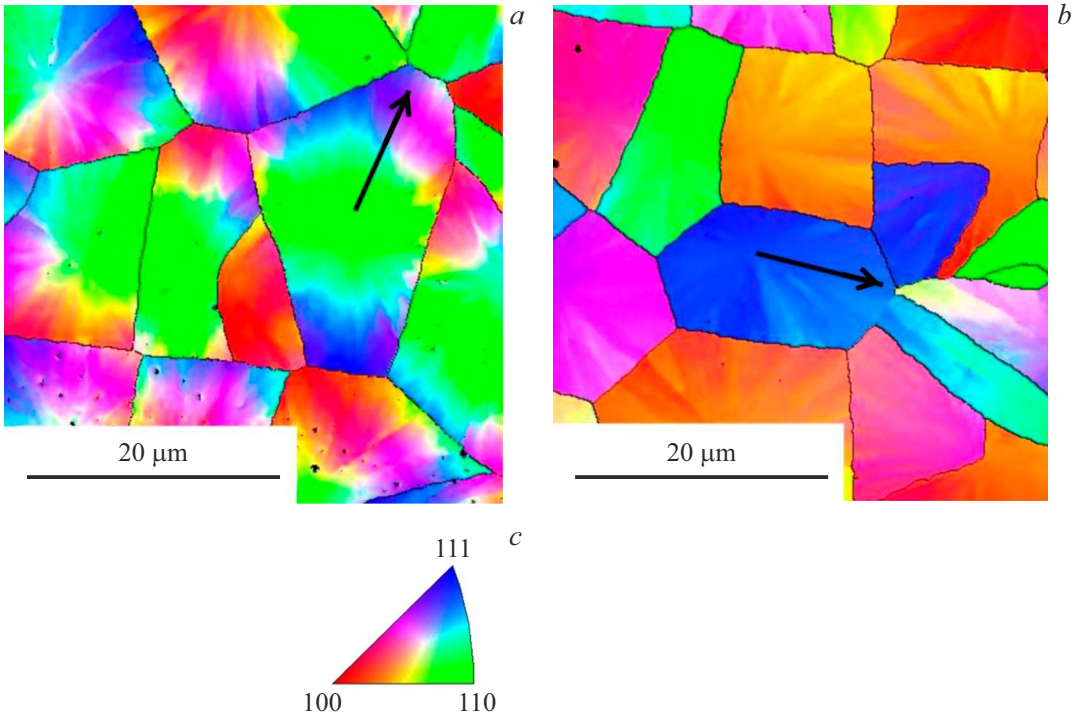


Figure 1. EBSD maps of 200-nm-thick (a) and 400-nm-thick (b) PZT thin films and color coding triangle (c) that illustrate growth orientations. A color version of the figure is provided in the online version of the paper.

in air at a temperature of 570 °C to form the perovskite structure. The layer thickness was varied within the 100−700 nm range. The angle of crystal lattice rotation was determined with a Lira3 Tescan scanning electron microscope in the electron backscatter diffraction (EBSD) mode. The energy of the probing beam was 20 keV.

Figures 1, a, b show characteristic EBSD maps of thin films with a thickness of 200 and 400 nm, which have a structure consisting of individual spherulitic blocks. Growth orientations ⟨100⟩, ⟨110⟩ and ⟨111⟩ correspond to the primary colors of the color coding triangle shown in Fig. 1, c. The linear dimensions of blocks vary within the 10−20 μm range. The color change in radial directions from the center of spherulites to their periphery reflects a change in orientation of the growth axis, which is indicative of crystal lattice rotation. It can be seen that the angle of lattice rotation (φ) varies monotonically (Fig. 2) along the chosen radial directions shown in Fig. 1. As the thickness increases, the rotation rate ($|\mathrm{grad}\varphi|$) decreases noticeably (curves *1* and *2* in Fig. 2).

Figure 3, a illustrates the variation of the lattice rotation rate averaged over the studied film area ($100 \times 100\,\mu$m) with an increase in thickness of submicrometer films. The curve indicates that the value of $|\mathrm{grad}\,\varphi|$ decreases by more than an order of magnitude (from ~ 6.5 deg/μm at $d = 100$ nm to ~ 0.4 deg/μm at $d = 700$ nm) within the studied thickness interval. In the former case, this implies that the growth axis orientation at a distance of $\sim 14\,\mu$m from the center of a spherulitic block changes by $\sim 90°$ (from normal to the substrate plane to an in-plane orientation). In the 700-nm-thick film, the magnitude of lattice rotation at the same distance did not exceed 6°.

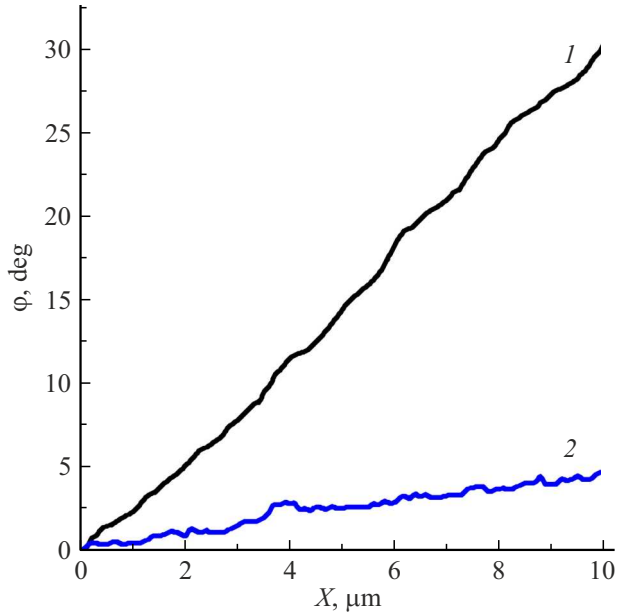


Figure 2. Variation of the angle of lattice rotation (φ) along the chosen radial directions (Fig. 1) from the center of blocks to their periphery for films with a thickness of 200 (*1*) and 400 nm (*2*).

The authors of several studies [3,4,7,8] have estimated the bending deformation in thin films using a formula that relates the cylinder deformation (ε) to the lattice rotation

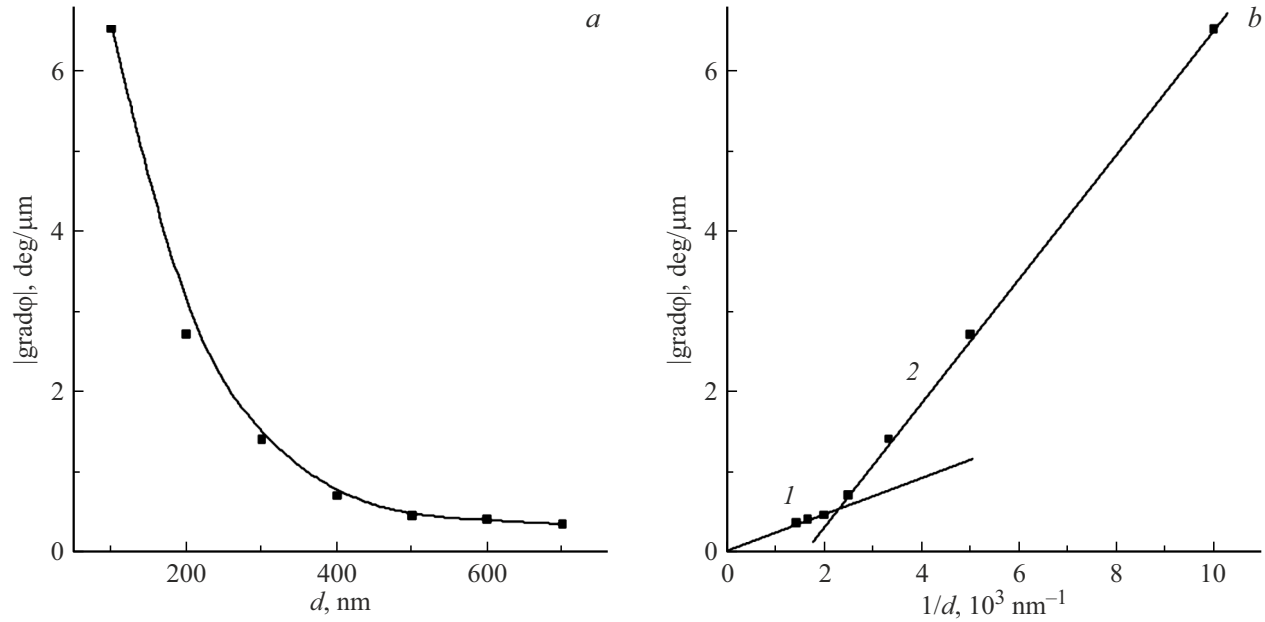


Figure 3. Variation of the average lattice rotation rate in PZT films with increasing thickness of these films (a) and dependence of the average lattice rotation rate on $1/d$ (b).

rate ($|\mathrm{grad}\,\varphi|$) and the thin layer thickness (d):

$$\varepsilon = \left|\mathrm{grad}\,\varphi\right| d/2. \quad (1)$$

It follows from this formula that the lattice rotation rate is inversely proportional to the deformed thin layer thickness, and the deformation itself is determined as the slope of this dependence

$$\left|\mathrm{grad}\,\varphi\right| = \varepsilon \cdot 2/d. \quad (2)$$

The corresponding experimental dependence is shown in Fig. 3, *b*. It is evident that it may be approximated by two linear sections *1* and *2*. Therefore, the magnitude of relative deformation, which is determined by the slope of the curve, remains virtually unchanged within each interval. It can be seen that the linear approximation of points at large film thicknesses (section *1*) tends to zero, which is apparently indicative of elastic nature of deformation (ε^e) within this thickness range; its magnitude was estimated based on the data in Fig. 3, *b* and formulae (1) and (2) as $\varepsilon^e = 0.2\,\%$. The linear approximation of points at smaller thicknesses (section *2*) crosses the ordinate axis at negative values of the lattice rotation angle. This may imply that elastic deformation ε^e in films is combined with inelastic (plastic) deformation (ε^i); their sum was estimated as $\varepsilon^e + \varepsilon^i = 0.75\,\%$. Thus, the magnitude of inelastic deformation was $\varepsilon^i = 0.55\,\%$.

One possible scenario of plastic deformation is disclination with the angle of lattice rotation changing abruptly when limiting magnitudes of elastic deformation are reached [6]. Another option is ferroelasticity of a thin PZT film with lateral stretching mechanical stresses inducing a reorientation of the spontaneous polarization vector in directions as close as possible to the substrate plane, which is accompanied by deformation of the crystal lattice. For example, the lattice deformation for a thin film composition approaching the morphotropic phase boundary from the tetragonal phase side is $\sim 1-2\,\%$ [17]. The lattice deformation for film compositions corresponding to the rhombohedral or monoclinic modification of the ferroelectric phase is expected to be of the same order of magnitude as the one for tetragonally deformed films. However, this issue warrants separate study.

Thus, the thickness dependence of the lattice rotation rate in submicrometer spherulitic PZT films with their thickness varying within the $100-700$ nm range has been studied for the first time by electron backscatter diffraction. The nature of this dependence indicates that plastic deformation is added to elastic one as the thickness decreases. The deformation magnitudes were estimated, and a mechanism for the emergence of plastic deformation was proposed. A thickness dependence of a similar nature is to be expected in other thin-film spherulitic materials of different compositions and crystal structures.

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Conflict of interest

The authors declare that they have no conflict of interest.

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