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# Radially oriented lateral self-polarization in spherulitic lead zirconate titanate thin films

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The lateral piezoelectric response and Kelvin mode of individual perovskite islands, distinguished by radial spherulitic microstructure, in lead zirconate titanate thin films were studied. It has been shown that spherulitic islands are radially polarized, which is associated with a change in phase density during crystallization of the perovskite phase from the low-temperature pyrochlore phase.

**Keywords:** lead zirconate titanate thin films, radially radiant spherulitic structure, piezoforce microscopy.

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Spherulitic crystalline structures are very common in nature. They are found in alloys, minerals, and organic compounds [1,2]. In thin films, spherulites may assume shapes close to those of a radial disk or more complex irregular figures [3–8]. The development of compact oscillators based on thin-film polar quartz ($SiO_2$) and quartz-like ($GeO_2$) materials has recently spurred the interest in such structures [3,4]. It was found experimentally that a radially radiant spherulitic microstructure forms in the course of high-temperature crystallization of amorphous quartzes predeposited onto a substrate. Blocks in such structures may be as large as several tens of micrometers in size. It was revealed by electron backscatter diffraction (EBSD) that the growth axis rotates (tilts) in the process of radial growth of a spherulite. According to [3,4], the radial axis rotation rate is as high as $0.5-0.7$ deg/$\mu$m.

A radially radiant microstructure is also typical of polycrystalline ferroelectric films prepared in two stages (deposition of amorphous films on a substrate with subsequent high-temperature annealing) with the use of both physical and chemical fabrication techniques. Specifically, a microstructure in the form of „rosettes“, which assumed the shape of nearly perfect circular disks in certain cases [8–11], was observed in thin films of lead zirconate titanate (PZT) that are regarded as essential materials for modern microelectromechanics [5–7]. The size of these disks varied from a fraction of a micrometer to several tens of micrometers depending on the technological conditions of thin-film growth. Our earlier studies have revealed that the mean size of spherulitic blocks forming in two-stage magnetron sputtering of a ceramic PZT target may be adjusted within a wide range (from several micrometers to tens of micrometers) by varying the target–substrate distance within the $70-30$ mm interval [11–13]. An anomalous enhancement of the second optical harmonic signal (by a factor of more than 20) was also observed in these studies [11,13]. Since the second optical harmonic signal is proportional to the square of projection of polarization normal to the incidence direction of optical radiation (i.e., lateral polarization), the lateral polarization value increased by a factor of more than 4. It was found in [12,13] that the growth axis rotates (tilts) toward the boundary of a spherulitic island (as in the case of crystallization of quartz spherulites) when the spherulite size grows. The rotation rate varies from 0.5 to 1 deg/$\mu$m with the size of spherulites. It was hypothesized in [14] that these changes are induced by tensile mechanical stresses in the film (substrate) plane, which emerge in the course of crystallization (accompanied by a change in the film density) of the perovskite phase from the pyrochlore phase. In view of this, the present study was aimed at examining the behavior of ferroelectric polarization in thin-film PZT spherulites by piezoresponse force microscopy.

A thin PZT film with a composition corresponding to the morphotropic phase boundary region (with elemental ratio Zr/Ti = 54/46) was grown on a sitall ST-50 substrate coated with platinum with an adhesion titanium underlayer. Radio-frequency magnetron sputtering of the ceramic target was performed at a low temperature corresponding to the temperature of substrate heating by gas plasma. The thickness of the deposited sample was 900 nm. In order to form individual perovskite spherulitic islands in a low-temperature pyrochlore matrix, the samples were annealed in air in a SUOL 0.3.2/12 furnace for 1 h at a temperature of 530°C.

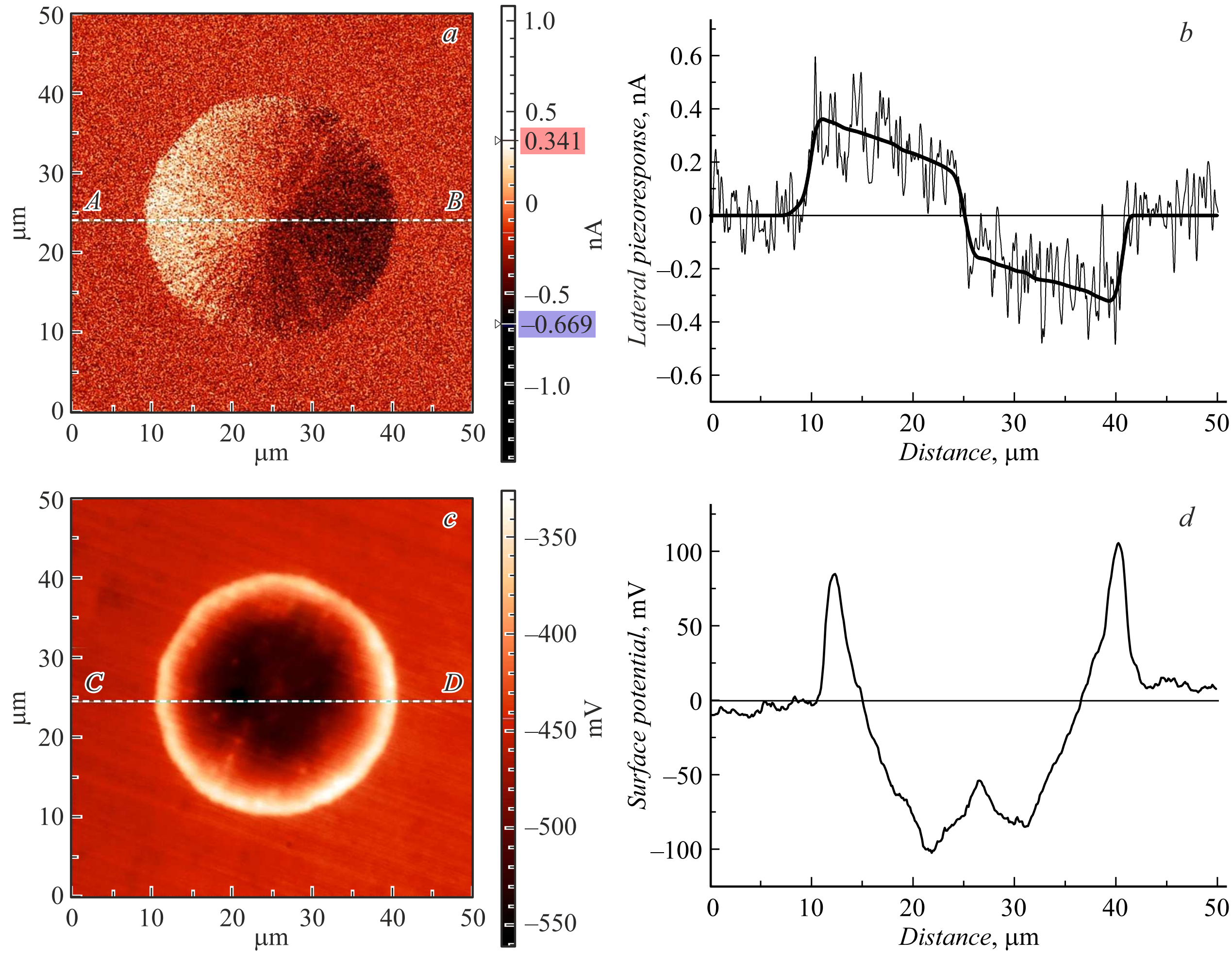


**Figure 1.** Lateral PFM image of a perovskite spherulitic island (*a*), distribution of the lateral signal within diametric section *A*−*B* (*b*), SKPM signal (Kelvin mode) (*c*), and its distribution within diametric section *C*−*D* (*d*).

The phase composition was monitored with a Lyra3 Tescan scanning electron microscope operated in the electron backscatter diffraction mode. The piezoresponse force microscopy (PFM) method was used to determine the lateral piezoresponse component. Measurements were carried out in the contact mode with AC voltage (5 V, 150 kHz) applied to the cantilever. The surface potential was determined by scanning Kelvin probe microscopy (SKPM). Measurements were performed with the use of MFP-3D SA (Asylum Research) and Ntegra Prima (NT-MDT SI, Russia) atomic force microscopes. The scanned surface area was $50 \times 50\,\mu$m.

Figure 1, *a* shows the PFM image of lateral piezoresponse of a radially radiant spherulitic island of a two-phase PZT film obtained after high-temperature annealing, while Fig. 1, *b* presents the distribution of this signal within diametric section *A*−*B*. It is evident that the distribution is distinctly non-uniform: the signal was near-zero at the spherulite center, but the piezoresponse signal intensified sharply to the right and to the left of the center and grew gradually with further shift toward the periphery of an island. The sign of the signal was reversed in passing through the spherulite center.

Figure 1, *c* presents the surface potential distribution (SKPM image). The Kelvin mode signal is radially non-uniform: the negative surface charge was concentrated in regions adjacent to the spherulite center and grew weaker toward the periphery. The sign of the SKPM signal was reversed in the vicinity of the perovskite−pyrochlore boundary (Fig. 1, *d*).

Figure 2 presents the result of processing of the *Z*-component (vertical component) of the EBSD signal and reveals an almost linear rotation of the growth axis away from the center of an island in the course of radial growth of a spherulite. The axis rotation rate ($\sim 1.5\,\text{deg}/\mu$m) was somewhat higher than the one observed in experiments into the growth of quartz spherulites [3,4].

This rotation is attributable to a 7−8% enhancement of the film density in the process of crystallization of the perovskite phase [3,4,14]. Both the axis rotation and the film shrinkage are induced by partial relaxation of mechanical stresses in the course of phase transformation.

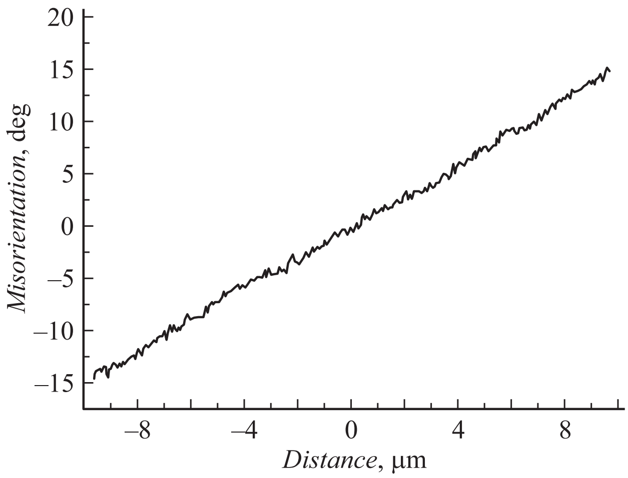


**Figure 2.** Diametric variation of the rotation angle of the growth axis in a radially radiant perovskite spherulitic structure.

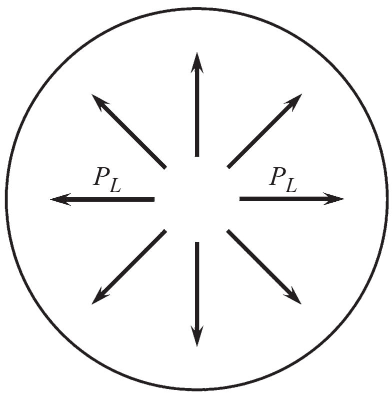


**Figure 3.** Schematic distribution of the lateral projection of ferroelectric polarization in a radially radiant spherulite.

Radial residual mechanical stresses apparently reorient the lateral component of ferroelectric polarization in the radial direction. The lateral piezoresponse image in Fig. 1, *a* is light to the left of the spherulite center and dark to the right of it, suggesting that the lateral polarization component is oriented from the center of an island to its periphery [15]. In other words, a spherulite island is a radially self-polarized formation that is shown schematically in Fig. 3.

A negative potential on the free surface of a spherulite may be induced by electrons localized at deep near-surface traps [16]. The sign change near the boundary between the perovskite spherulitic structure and the pyrochlore phase is apparently associated with lateral polarization: its vector is oriented radially toward the island boundary, thus producing an uncompensated positive charge.

Thus, it was demonstrated that mechanical stresses emerging as a result of solid-phase crystallization of radially radiant perovskite spherulitic structures apparently trigger rotation of the growth axis in the radial direction and induce the formation of a somewhat unique object: a radially polarized spherulite. Similar to the macroscopic vertical polarization component (self-polarization), the lateral polarization component oriented in the radial direction may be called radial (lateral) self-polarization.

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## Conflict of interest

The authors declare that they have no conflict of interest.

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