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Spherulitic microstructure of thin PZT films

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Abstract. The paper shows that the formation of a radiant spherulites microstructure in lead zirconate-titanate thin films obtained by radio-frequency magnetron sputtering is associated with the formation of radial tensile mechanical stresses acting in the substrate plane, the magnitude of which increases with increasing linear size of spherulites. It leads to a change in the lattice parameter of the perovskite structure and the appearance of induced polarization, the value of which can significantly exceed the spontaneous polarization.

Keywords: PZT thin films, spherulitic microstructure, optical second harmonic generation, mechanical stresses, induced polarization

Introduction

Around us, spherulitic crystal structures are widespread in the organic and inorganic nature. The first works on the study of their structure and formation mechanisms were started in the first half of the 19th century by Talbot, Brewster (Brewster 1815; 1853; Talbot 1837) and somewhat later by a number of other researchers (Cross 1891). The types of spherulitic structures are well classified and vary greatly in growth pattern and microstructure. Spherulites are widely represented in minerals, as a rule, in the form of balls of a radially radiant structure (Kantor 1997; Shtukenberg et al 2012).

The current attention to spherulites is associated, in particular, with the development of miniature piezoelectric quartz oscillators, which require the use of thin-film technologies for their manufacture (Lutjes et al. 2021; Musterman et al. 2022). Practice has shown that the process of crystallization of quartz films from a glassy phase is difficult to control, and the films themselves often take the form of radiant spherulites (Lutjes et al. 2021; Musterman et al. 2022). As experiments have shown, one of the features of radiant spherulites is the rotation of the growth axis during the radial growth of spherulites (from the center to the periphery), which leads to structural disturbances and, apparently, negatively affects the oscillatory properties of the grown films.

It turned out that the spherulitic microstructure is widespread in thin polycrystalline films, including lead zirconate titanate (PZT) films (Alkoy et al. 2007; Klee et al. 1994; Preston, Haertling 1992; Pronin et al. 2018), which are increasingly used in microelectromechanical and infrared technology devices (Izyumskaya et al. 2007; Muralt et al. 2009; Song et al. 2021). However, there are practically no studies of the influence of the microstructure of films on their physical properties. The relevance of these studies is evidenced, however, by the fact that in thin PZT films in a narrow region of the morphotropic phase boundary (MPB), anomalously high electromechanical and piezoelectric parameters are observed, and it is obvious that a change in the microstructure of films can most decisively affect their physical characteristics. We carried out the first studies in this direction in previous years and found anomalous changes in the signal of the second optical harmonic (Elshin et al. 2020) and changes in the dielectric characteristics (Dolgintsev et al. 2021). The purpose of this work was to elucidate the possible causes of such anomalies in thin films of PZT.

Sample preparation and research methods

Samples of thin films were obtained using a two-stage method of radio-frequency magnetron sputtering and varying the distance from the target to the substrate. The substrate was a platinized silicon wafer. The thickness of the PZT films was nearly 500 nm, and the composition corresponded to the MPB region. In our previous works (Dolgintsev et al. 2021; Elshin at al. 2020), the technology for obtaining samples is described in more detail. Both single-phase perovskite films formed at 580 °C and films formed at 550 °C in which islands of the perovskite phase were formed in the matrix of the low-temperature pyrochlore phase were prepared.

To study the phase state, microstructure, and physical properties of thin films, we used a scanning electron microscope (SEM, EVO-40, Zeiss), an optical microscope Nikon Eclipse LV 150 as well as the method of nonlinear optical microscopy, which is informative for studying phase transitions and domain structures. The method is based on the analysis of the second optical harmonic signal (SHG), which is proportional to the square of the ferroelectric polarization oriented normally to the direction of propagation of the incident optical beam (Wang et al. 2017).

The second optical harmonic was excited by femtosecond laser radiation with a wavelength of 800 nm, a repetition rate of 80 MHz, and a duration of 100 fs. The SHG intensity was recorded at a wavelength of 400 nm. The plane of polarization of the incident beam was rotated by a half-wave plate in front of the sample. A Glan prism was used as an analyzer. The images were fixed in the "reflection" geometry. The Zeiss N-achroplan 100X objective of the WITec alpha 300S confocal microscope provided a spot on the sample with a diameter of 0.9 μm, and the use of an optical fiber provided a spatial resolution of ~300 nm.

Experimental results and discussion

Images of individual perovskite islands are shown in Fig. 1. Fig. 1a is a SEM image obtained in the backscattered electron mode (the energy of the incident beam is 12 keV), and Figs. 1b and 1c are SHG images obtained for two polarization directions of the incident beam, differing by 90 degrees. It can be seen that the perovskite islands are almost round in shape and are characterized by a radially radiant spherulitic microstructure. The microstructure of the inner part of the spherulite strongly differs from the periphery. This difference is especially pronounced in SHG images, where the boundary between these regions is clearly visible.

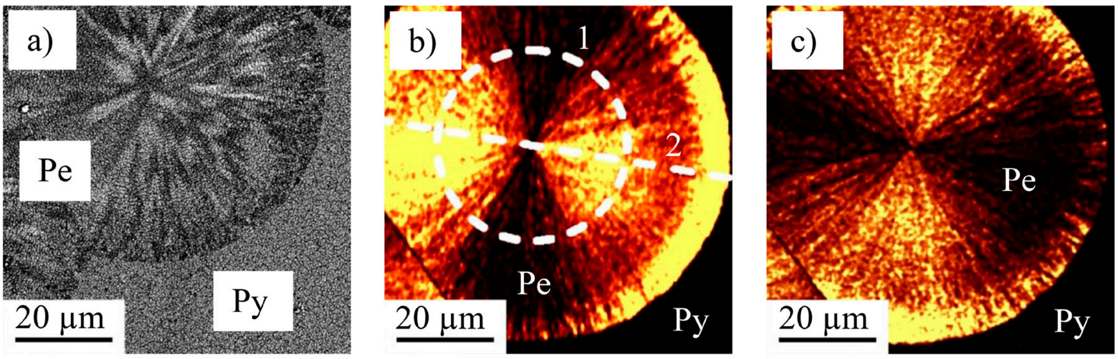

Fig. 1. SEM (a) and nonlinear optical images (b, c) of perovskite (Pe) islands in a pyrochlore (Py) matrix. Dotted lines in Fig. 1b show the diametrical and circular cross sections (1, 2)

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Fig. 2 is a diametrical cross section (line 1 in Fig. 1b) of the distribution of the SHG signal. Its value increases at the edges of the spherulite by a factor of ~2 compared to the signal in the central region. This behavior may indicate the formation of a radially radiant microstructure during the crystallization of the perovskite phase from the low-temperature pyrochlore phase through the intermediate perovskite phase, which is characterized by lower density. A similar nature of the recrystallization of the perovskite phase was observed earlier for perovskite spherulites, which differ in stepwise growth (Pronin et al. 2010).

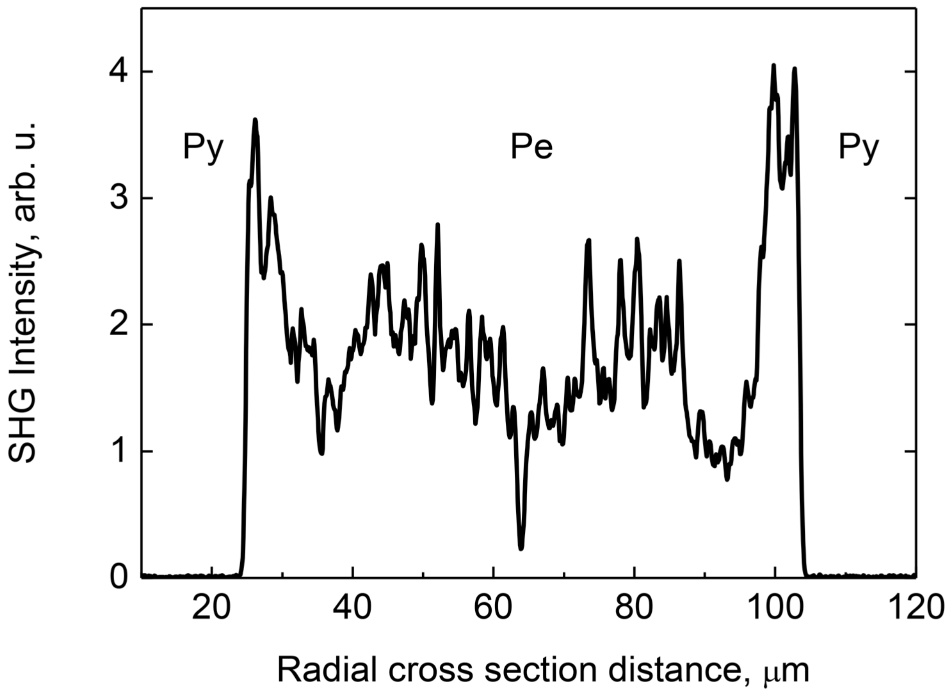

Fig. 2. Distribution of the SHG signal over section 1 in Fig. 1b spherulitic island

A distinct drop in the SHG signal at the interface between two modifications of perovskite phases (dense and loose) indicates that either the growth orientation and, as a consequence, the polarization orientation (with respect to the film plane) can differ greatly in these phases, while maintaining the same spatial symmetry of the ferroelectric phase, or the boundary is the region of phase transformation of the ferroelectric phase. So far, this question has not been answered and requires further research.

In Fig. 2, attention is also drawn to the near-sinusoidal change in the SHG signal, at which the signal is minimal in the center of the island, then, when moving away from the center, it first increases, reaching a local maximum approximately at the middle of the radius, and then decreases towards the edge. In other words, there is a radial "rotation" of the polarization vector. According to the results of the recent studies, in radiant spherulites, a rotation of the growth axis is observed with increasing spherulite radius (Elshin et al. 2023; Lutjes et al. 2021), which can lead to a change in the lateral polarization projection. However, additional studies are also required to confirm this assumption.

Fig. 3 reflects the change in the SHG signal over the circular cross section (marked by number 2 in Fig. 1b) for two directions of linear polarization of the incident beam, which differ by 90 degrees. It can be seen that the circular cross sections for a fixed polarization direction have two maxima. The obtained result suggests a correlation between the orientation of the polarization of the incident optical radiation and the orientation of the polarization vector in a ferroelectric film.

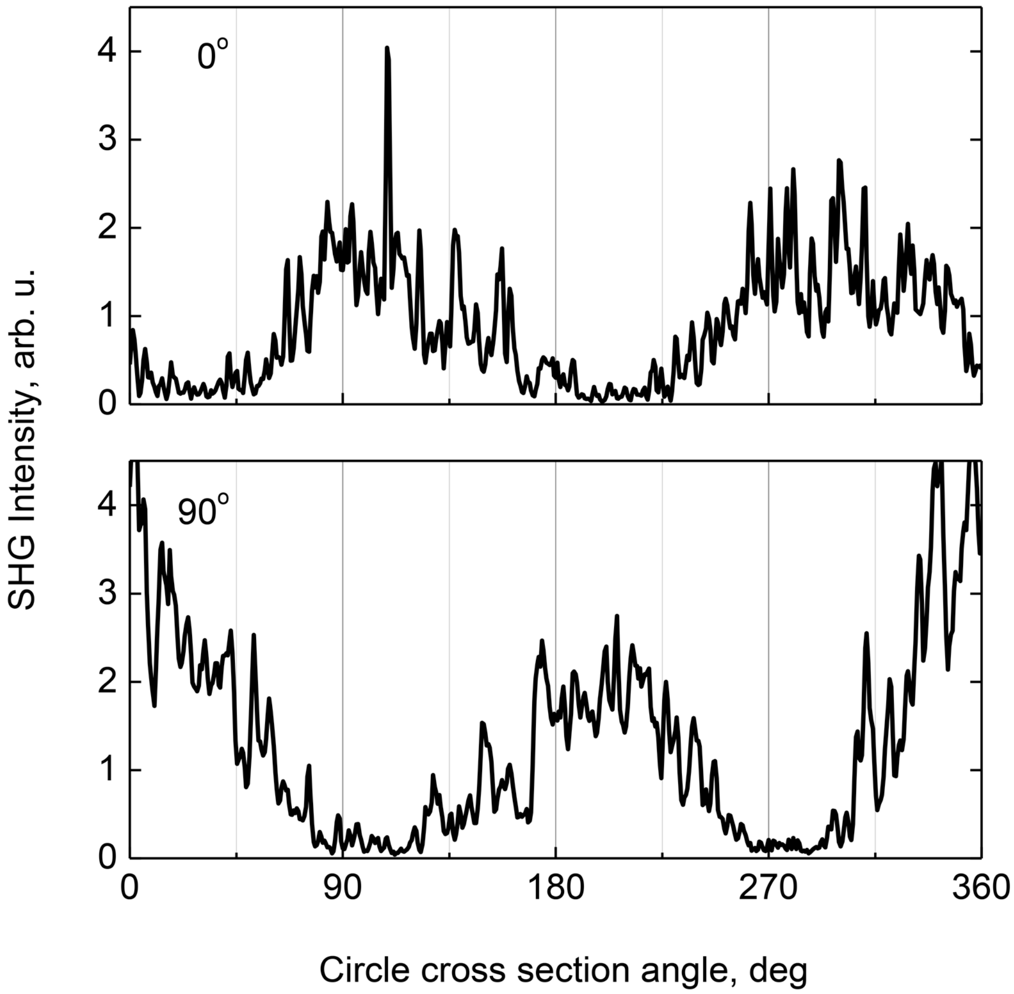

Fig. 3. Distribution of the SHG signals over circular section 2 (Fig. 1b) of a spherulite island of the incident beams with linear polarization differing by 90 °C

The observed result suggests that the cause of the collinearity of the optical polarization vector and the polarization vector in the spherulite may be radial mechanical stresses during the growth of the spherulite island. According to (Kukushkin et al. 2012), such radial mechanical stresses are caused by the difference in the density of the perovskite and pyrochlore phases at perovskite phase crystallization. Since the density of the pyrochlore phase is lower than the density of the perovskite phase, the perovskite island will be subjected to radial tension from the side of the pyrochlore matrix, which will lead to the appearance of a mechanically induced radially oriented polarization. Thus, the observed increase in the SHG signal at the periphery of the spherulitic island can be associated with a greater susceptibility to polarization reorientation in the region of the porous periphery relative to the denser central part of the island.

On Fig. 4, the left column shows the SHG images, and the right column shows the SEM images of single-phase PZT films deposited at different distances from the target to the substrate (at 40 and 70 mm) and different temperatures of the substrate heating by plasma (145 °C and 90 °C, respectively). It is clearly seen that a change in the technological parameters of film deposition leads to significant changes in the size and nature of the microstructure of spherulitic blocks as well as in the SHG signal (Table 1). It can be seen from Table 1 that a decrease in the film deposition temperature leads to a sharp change in the concentration of block spherulites, the number of which increases by almost an order of magnitude, the pseudocubic lattice parameter decreases, and the SHG signal increases by about 20 times.

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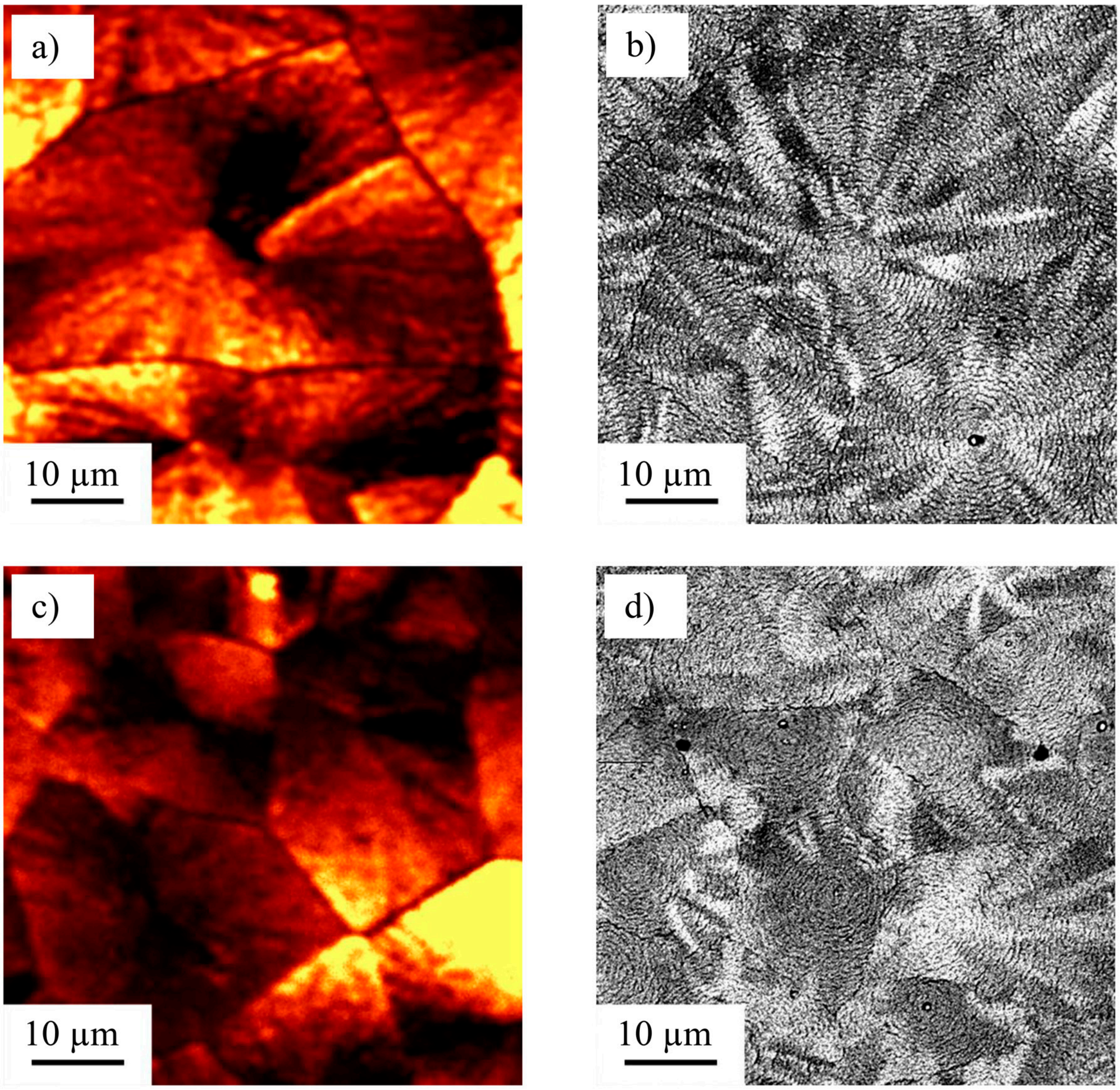

Fig. 4. Nonlinear optical and SEM images of PZT films deposited at different distances from the target to the substrate: d = 30 mm (a, b) and 70 mm (c, d)

Table 1. Changes in a number of technological, structural, and optical parameters of thin PZT films deposited at different distances from the target to the substrate

Distance from substrate to target, mm	Deposition temperature, °C	Block concentration, 10^2/mm^2	SHG signal, relat. un.	Pseudocubic lattice parameter, nm
40	145	9	45	0.40677
70	90	70	17	0.40738

The obtained data suggest that the anomalously high SHG signal in the film obtained at a distance from the target to the substrate of 40 mm is associated with an increase in tensile mechanical stresses, which increase with an increase in the linear dimensions of the spherulite blocks. In turn, these mechanical stresses induce an anomalously high polarization in the film plane, the value of which can be several times greater than the spontaneous polarization characteristic of a PZT film.

Conclusions

The analysis of the results obtained in this work allows us to conclude that in PZT films with a spherulite microstructure, the anomalous SHG signal is induced by radial mechanical stresses, the magnitude of which increases with the linear size of the spherulites. Estimates of the polarization show that it can exceed the spontaneous ferroelectric polarization by several times. It was found that the formation of a radiant spherulitic microstructure with a perovskite structure from a low-temperature nonpolar pyrochlore phase occurs in two stages, with the formation of a loose intermediate perovskite phase.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Authors contribution

The authors have made an equal contribution to the preparation of the paper.

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