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An influence of mechanical stresses on the phase state of spherulitic thin films of lead zirconate titanate

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ABSTRACT

The influence of lateral mechanical stresses on the crystal structure, microstructure and dielectric properties of spherulitic thin films of lead zirconate titanate is studied. The composition of lead zirconate titanate corresponded to the region of the morphotropic phase boundary. In thin films, the perovskite phase was formed during high-temperature annealing of amorphous films deposited by RF magnetron sputtering of a ceramic target on a cold silicon substrate. The deformation of the crystal lattice caused by the change in density during crystallization of the perovskite phase in the films changed with an increase in the area of spherulitic blocks with a variation in the target-substrate distance during their deposition. An increase in mechanical stress led to a linear rotation of the crystal lattice and a change in its parameters, as well as to a change in the microstructure of thin films. Based on the temperature dependences of the reverse dielectric permittivity, changes in the temperature of structural phase transitions in the films were revealed.

KEYWORDS

lead zirconate titanate thin films • morphotropic phase boundary • spherulitic microstructure • mechanical stresses

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Introduction

In recent years, an interest in thin films with spherulitic structure has been caused by both their increasing use in various practical applications and the development of multi-stage technologies based on the deposition of amorphous films at low temperatures and their subsequent multi-stage heat treatment. During heat treatment, crystallization of the films occurs through the formation of individual islands, which often take on a shape close to round, and are therefore called spherulites. The formation of a spherulitic microstructure is accompanied by an increase in the density of the films. The consequence of this is their shrinkage, which leads to a partial relaxation of lateral mechanical stresses acting from the amorphous or low-temperature intermediate phase. A similar situation is realized both in thin-film metals and alloys, and in semiconductor and dielectric films [1–8].

Since the change in the density of films during their crystallization can reach several percent, the formation of spherulites is accompanied by the appearance of strong lateral mechanical stresses and strain, Fig. 1. Thus, in hematite films (α-Fe_2O_3), the strain, estimated at ~ 0.5%, was accompanied by rotation of the growth axis, the rotation speed of which reached ~ 100 deg/μm [3]. In this regard, such crystal structures are often called transrotational [3,4] or simply rotational, when the rotation speed was lower and amounted to fractions or units of deg/μm [5–8].

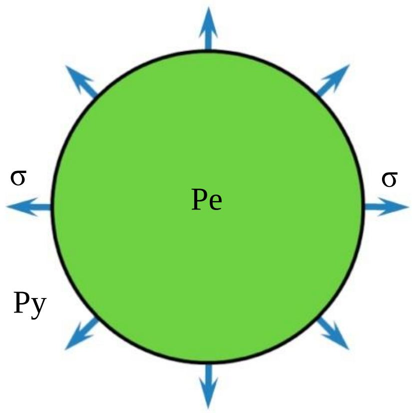

Fig. 1. Schematic representation of the effect of lateral mechanical stresses on a perovskite (Pe) two-dimensional island from the pyrochlore (Py) matrix

Until recently, the physical properties of rotational crystals have been practically unexplored, were mainly descriptive in nature and focused on the study of their microstructure features. There is even less information regarding thin ferroelectric films, primarily lead zirconate titanate (PZT) films, which are currently the main materials in microelectromechanics [9]. As a rule, everything was reduced to recording and describing the features of the spherulitic microstructure, without studying the nature of their formation and the role of mechanical stresses [10–14].

The development of new microscopic research methods, such as scanning electron microscopy, piezoresponse force microscopy, and second optical harmonic generation, have allowed a number of new results to be obtained in the study of thin-film spherulites. Thus, effects of lateral-radial self-polarization, an abnormally high second optical harmonic signal, and recrystallization of the perovskite phase were discovered in PZT thin films [15–17]. In addition, the phenomenon of electron channeling was discovered in InSiO and PZT films [7,18]. The objective of this work was to study the influence of mechanical stresses on the phase state of spherulitic thin PZT films, the composition of which corresponds to the region of the morphotropic phase boundary (MPB).

Interest in the phase state of PZT solid solutions in the region of coexistence of rhombohedral (R) and tetragonal (T) modifications of the ferroelectric phase (morphotropic phase boundary) is associated with anomalously high values of electromechanical and dielectric parameters, due to which ceramic materials based on PZT have remained the main materials of piezoelectric engineering over the past 70 years [19,20]. Thin PZT films find wider application both in microelectromechanics and in microwave electronics, non-volatile memory, photonics, IR technology, etc. [9,21–24]. At the same time, the nature of the anomalously high technical parameters remains not entirely clear, and the phase diagram of PZT has been refined over the years and is becoming increasingly complex. Figure 2 reflects one of the most widespread modern concepts of the MPB, in the region of which the existence of an intermediate ferroelectric modification of the monoclinic phase (M-phase) at low temperature and its coexistence with the tetragonal modification above room temperature (shaded area in Fig. 2) are assumed. Significantly below room temperature, there is a phase boundary that is responsible for the phase transition associated with either parallel or antiparallel rotation of the octahedra along one or more orthogonal axes of the cube [19,25,26]. In a number of other works, for example in [27], a whole cascade of phase transformations of various modifications of the ferroelectric phase is assumed in the field of MPB.

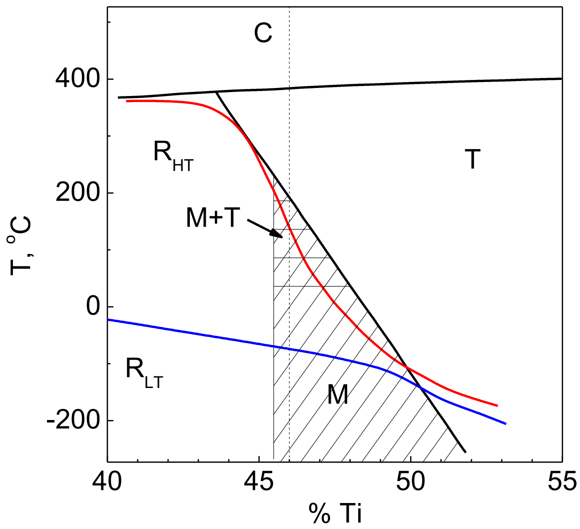

Fig. 2. Phase diagram of PZT solid solutions in the region of the morphotropic phase boundary, according to [19,24,25]

The phase diagram of thin PZT films in the MPB region can be even more complex, which is associated not only with the features of crystallization of the spherulitic structure of films from the amorphous phase, but also with the mechanical impact on the film from the substrate and intermediate sublayers [28,29]. According to theoretical calculations performed for epitaxial thin PZT films [30], mechanical stresses lead both to a shift toward an increase in the Curie temperature and to an expansion of the stable state of the monoclinic modification of the ferroelectric phase in the MPB region.

Materials and Methods

To identify the role of mechanical stresses associated with a decrease in their volume during the crystallization of the perovskite phase, thin films deposited from a ceramic target of the $PbZr_{0.54}Ti_{0.46}O_3$ composition corresponding to the region of the MPB using a two-stage method of RF magnetron sputtering were studied. Films with a thickness of about 500 nm were deposited at different target-substrate distances ($D_{T\text{-}S}$) in the range of 30–70 mm and, as a consequence, differed in the temperature of the substrate heated by plasma (90–160 °C), as well as in the average size of spherulitic blocks (15–40 μm) formed by high-temperature annealing at 580 °C [16,31]. The films structure was studied using scanning electron microscopy in the electron backscatter mode and electron backscatter diffraction mode (Lira 3 Tescan, EVO-40 Zeiss), X-ray phase analysis θ-2θ (Rigaku Ultima IV), and optical microscopy (Nikon Eclipse LV150). An E7-20 immittance meter and a modified Sawyer-Tower scheme were used to study the dielectric properties.

Results and Discussion

Optical and phase analysis of the formed PZT films showed the absence of parasitic phases, and the presence of all the main reflections of the perovskite phase in the diffraction pattern indicated the polycrystalline nature of the crystalline structure (Fig. 3(a)). In the absence of reflection splitting, it was not possible to identify the symmetry of the ferroelectric phase. Figure 3(b) shows the dependence of the change in the lattice parameter of the perovskite structure under the assumption of pseudocubic symmetry, from which it is evident that the lattice parameter changes abruptly with a decrease in the target-substrate distance from 60 to 50 mm. Figure 3(c) demonstrates the change in the full width at half maximum (FWHM) of the (110) peak, which experiences a jump and correlates with the lattice parameter behavior.

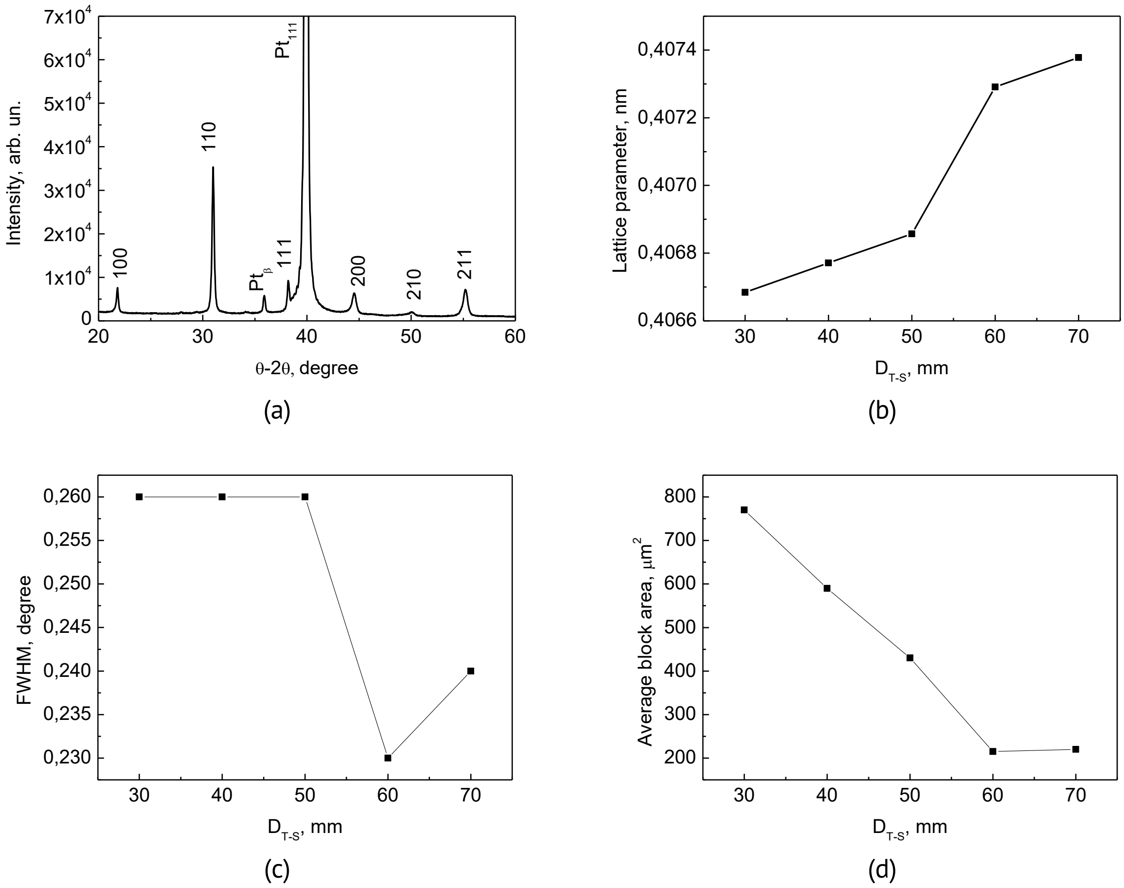

Fig. 3. Typical θ-2θ X-ray diffraction pattern of PZT thin films (a), change in the pseudocubic lattice parameter (b), change in the FWHM of the (110) reflex (c) and the average area of spherulitic blocks (d)

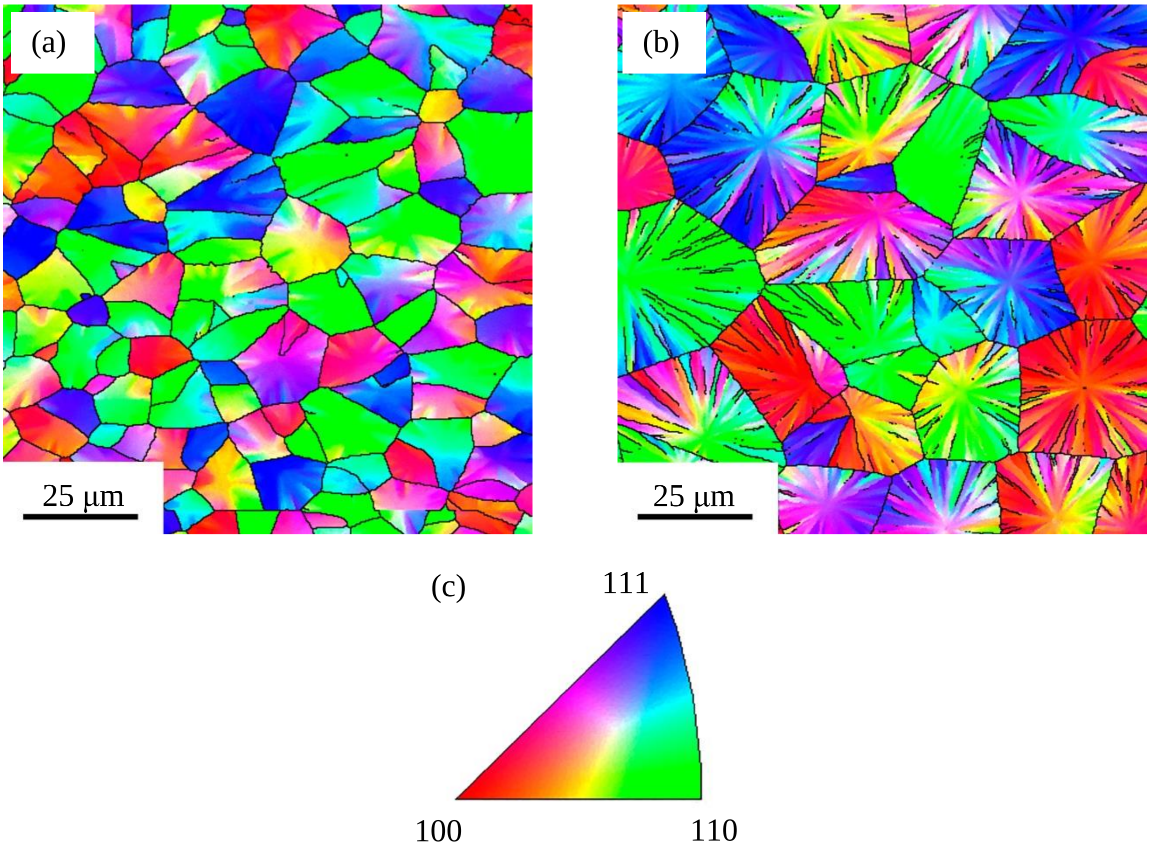

Fig. 4. Crystallographic orientation maps of growth axes of thin films deposited at $D_{T\text{-}S}$ of 30 mm (a) and 60 mm (b), as well as color coding of growth axes orientations (c)

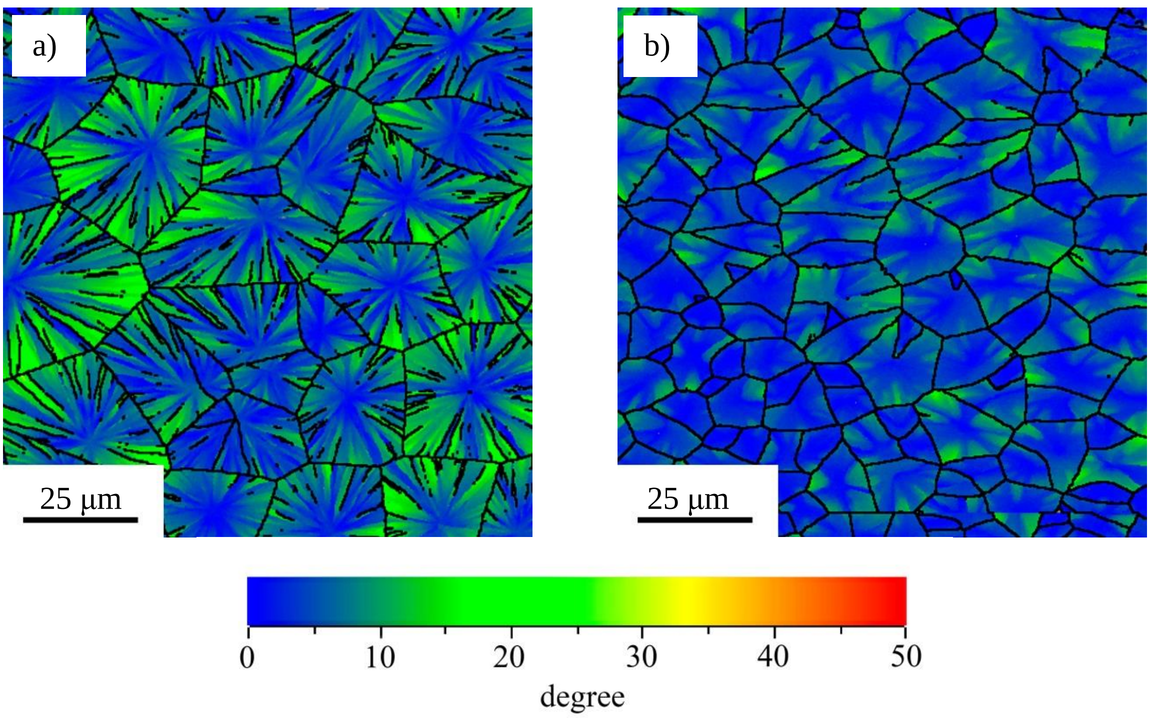

Fig. 5. GROD maps of thin spherulitic films deposited at target-substrate distances of 30 mm (a) and 60 mm (b)

High-temperature annealing of the deposited amorphous films resulted in the nucleation and growth of spherulitic islands of the perovskite phase, which formed a block structure during further growth. Electron images of spherulitic blocks, shown in Fig. 4(a,b), reflect a radially radiant microstructure. The block area increased with decreasing target-substrate distance, and this change correlated with the behavior of the lattice parameter (Fig. 3(d)). The electron backscatter diffraction maps confirm the polycrystalline nature of the spherulitic films, characterized by a predominant <110> growth texture.

Figure 5 shows GROD (Grain Reference Orientation Deviation) maps constructed based on the analysis of electron backscatter diffraction data, in which the change in color scale characterizes the rate of rotation of the crystal lattice.

Flowing radial color change within a single block or ray (Fig. 6(a)) indicates a monotonous and close to linear radial rotation of the crystal lattice from the center to its block periphery (Fig. 6(b)). The range of the rotation rate of crystal lattice of the samples studied was ~ 0.5–1.5 deg/μm. Thus, the obtained data indicate strain of the crystal lattice as a result of its rotation. Since the rotation of the crystal lattice occurs with the formation of dislocations, a partial relaxation of radial mechanical stresses takes place [5]. Similarly, partial relaxation of tangential component of mechanical stresses occurs with the appearance of radial boudaries (Fig. 4(b)).

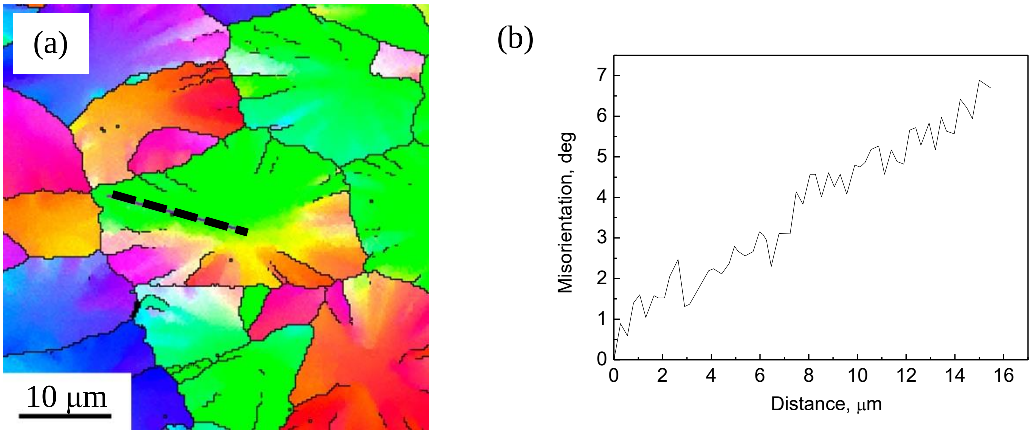

Fig. 6. Radial rotation of the crystal lattice in a spherulitic block in the direction indicated by the dotted line

As a first approximation, the maximum strain can be estimated using the equation for the strain of a flat cylinder:

$\varepsilon = |\mathrm{grad}\ \varphi|\ t/2$, (1),

where ε is the relative strain, t is the film thickness, φ is the rotation angle [2]. According to the obtained results, the estimate of the maximum value of ε varies in the range of 0.25–0.75 %.

The magnitude of mechanical stresses:

$\sigma = E\varepsilon$, (2),

where E is Young's modulus (equal to 115 GPa [32]), lies in the range of ~ 300–900 MPa, while the elastic limit for thin PZT films, according to [33], is ~ 500 MPa. Since the rotation of the crystal lattice occurs with partial relaxation of mechanical stresses [5], it is assumed that the actual residual stresses may be significantly less. However, for their accurate assessment, additional microscopic studies and an adequate model are necessary.

The study of the temperature dependences of the dielectric permittivity χ(T) made it possible to analyze and evaluate the phase state with a change in the target-substrate distance and the crystalline parameters of thin films. Figure 7 shows the temperature dependences of the reciprocal value of the permittivity (1/*χ*), a change in the slope of which may indicate a phase transformation from one modification of the ferroelectric phase to another [34]. As can be seen from the graphs, in the range of 20–300 °C (at the Curie temperature TC ~ 380–400 °C) in all the studied samples, two distinct changes in the slope on the 1/*χ*(*T*) curve were observed - the phase transition PT-1 (curve 1) and the phase transition PT-2 (curve 2), the temperatures of which changed noticeably with variations in the target-substrate distance.

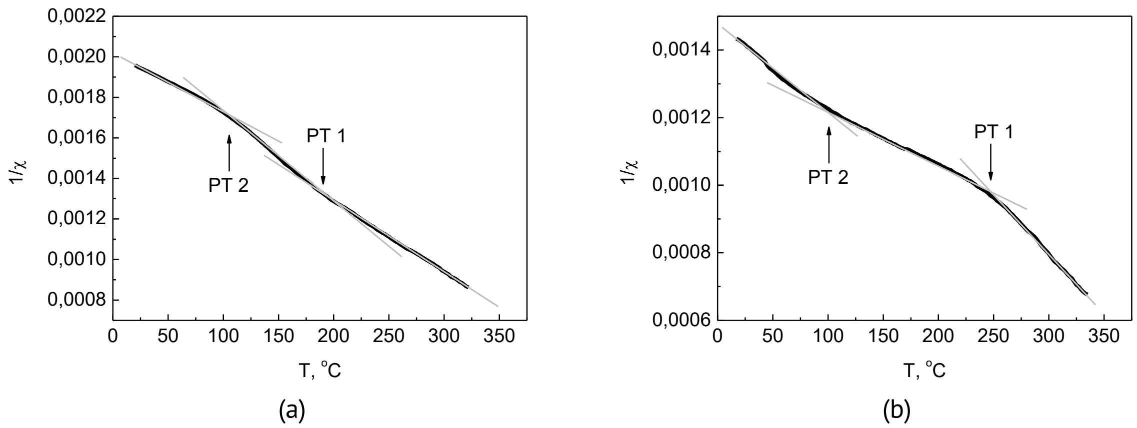

Fig. 7. Temperature dependences of the reciprocal dielectric permittivity (1/*χ*) for PZT thin films deposited at $D_{S\text{-}T}$ of 30 mm (a) and 70 mm (b)

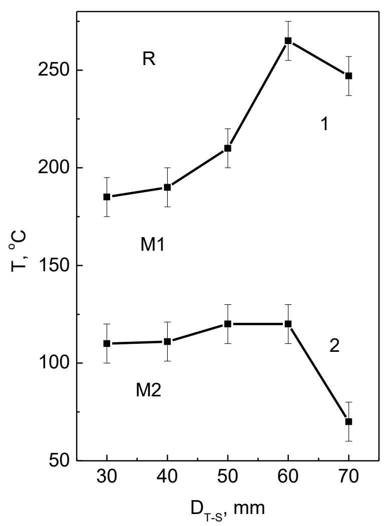

Fig. 8. Phase diagram of spherulitic thin films with changing target-substrate distance

These changes are reflected in Fig. 8. It is evident that with an increase in the size of the spherulitic blocks (and mechanical stresses), the temperature of PT-1 decreases noticeably, which correlates with the phase boundary on the *T*-*ε* phase diagram in thin PZT films, which reflects the phase transformation from the ferroelectric rhombohedral phase to the monoclinic (R→M1) ferroelectric phase with an increase in the deformation of the crystal lattice *ε* [29].

The interpretation of the low-temperature phase transition (M1→M2) (curve 2) in the films under study is associated with the presence of a phase transition associated with the rotation of oxygen octahedra. Such perovskite structures are observed in calcium titanate perovskite $CaTiO_3$ or in the low-temperature phase of strontium titanate $SrTiO_3$. In ceramic PZT solid solutions in the region of MPB, this phase transition is located below room temperature (Fig. 2). We believe the presence of strong mechanical stresses in PZT spherulitic films shifts this phase transition to the region toward higher temperatures by ~ 150 °C or more. To confirm the version, additional studies using highly sensitive X-ray equipment and a number of new structural methods are needed.

Conclusion

The paper studies spherulitic thin PZT films of composition corresponding to the morphotropic phase boundary, which were produced by a two-stage method, including RF magnetron sputtering of a ceramic target onto a platinized silicon substrate (1) and subsequent high-temperature annealing of the films in air (2). It is shown that a decrease in the target-substrate distance leads to an increase in the size of the spherulitic blocks, which in turn leads to a change in the parameters of the crystal lattice, a linear increase in its radial rotation, and an increase in the rotation rate.

The observed changes confirm the previously made assumptions about the role of tensile mechanical stresses in the plane of a spherulitic thin film, arising due to the difference in the densities of the amorphous and crystalline phases. In our case, in thin PZT films, the difference lies in the crystallization of the perovskite phase from the low-temperature intermediate pyrochlore phase. The values of mechanical stresses are estimated, the values of which either reach or exceed the elastic limit of thin PZT films.

Analysis of the slope changes in the temperature dependences of the reciprocal dielectric permittivity caused by a change in the phase state of thin films made it possible to reveal the relationship between mechanical stresses and temperature changes in structural phase transitions occurring in thin PZT films in the region of the morphotropic phase boundary.

References

1. Shtukenberg AG, Punin YO, Gunn E, Kahr B. Spherulites. *Chemical Reviews.* 2012;112(3): 1805–1838.
2. Kolosov VYu, Thölén AR. Transmission electron microscopy studies of the specific structure of crystals formed by phase transition in iron oxide amorphous films. *Acta Materialia.* 2000;48: 1829–1840.
3. Zhigalina OM, Khmelenin DN, Valieva YA, Kolosov VYu, Kuznetsov KA, Bokunyaeva AO, Vorotilov KA, Sigov AS. Structural features of PLZT films. *Crystallography Reports.* 2018;63(4): 646–655.
4. Kooi BJ, De Hosson JThM. On the crystallization of thin films composed of Sb3.6Te with Ge for rewritable data storage. *Journal of Applied Physics.* 2004;95(9): 4714–4721.

5. Lutjes NR, Zhou S, Antoja-Lleonart J, Noheda B, Ocelík V. Spherulitic and rotational crystal growth of Quartz thin films. *Scientific Reports.* 2021;11(1): 14888.
6. Musterman EJ, Dierolf V, Jain H. Curved lattices of crystals formed in glass. *International Journal of Applied Glass Science.* 2022;13(3): 402–419.
7. Da B, Cheng L, Liu X, Shigeto K, Tsukagoshi K, Nabatame T, Ding Z, Sun Y, Hu J, Liu J, Tang D, Zhang H, Gao Z, Guo H, Yoshikawa H, Tanuma S. Cylindrically symmetric rotating crystals observed in crystallization process of InSiO film. *Science and Technology of Advanced Materials: Methods.* 2023;3(1): 2230870.
8. Sun W, Zhou W. Growth mechanism and microstructures of Cu2O/PVP spherulites. *RSC Advances.* 2022;12: 20022.
9. Song L, Glinsek S, Defay E. Toward low-temperature processing of lead zirconate titanate thin films: Advances, strategies, and applications. *Applied Physics Reviews.* 2021;8(4): 041315.
10. Spierings GACM, Van Zon JBA, Larsen P K, Klee M. Influence of platinum-based electrodes on the microstructure of sol - gel and MOD prepared lead zirconate titanate films. *Integrated Ferroelectrics.* 1993;3(3): 283–292.
11. Nashimoto K, Nakamura S. Preparation and characterization of sol-gel derived epitaxial and oriented Pb(Zr0.52Ti0.48)O3 thin films. *Japanese Journal of Applied Physics.* 1994;33(9S): 5147–5150.
12. Chen S-Y, Chen I-W. Texture development, microstructure evolution, and crystallization of chemically derived PZT thin films. *Journal of American Ceramic Society.* 1998;81(1): 97–105.
13. Alkoy EM, Alkoy S, Shiosaki T. The effect of crystallographic orientation and solution aging on the electrical properties of sol-gel derived Pb(Zr0.45Ti0.55)O3 thin films. *Ceramic International.* 2007;33: 1455–1462.
14. Bretos I, Rodrigez-Castellon E, Tomczyk M, Jimenez R, Vilarinho PM, Calzada ML. Active layers of high-performance lead zirconate titanate at temperatures compatib le with silico-nano- and microelecrtonic devices. *Scientific Reports.* 2016;6: 20143.
15. Elshin AS, Pronin IP, Senkevich SV, Mishina ED. Nonlinear optical diagnostics of thin polycrystalline lead zirconate titanate films. *Technical Physics Letters.* 2020;46(4): 385–388.
16. Staritsyn MV, Pronin VP, Khinich II, Senkevich SV, Kaptelov EYu, Pronin IP, Elshin AS, Mishina ED. Microstructure of spherulitic lead zirconate titanate thin films. *Physics of the Solid State.* 2023;65(8): 1312–1318.
17. Kiselev DA, Staritsyn MV, Senkevich SV, Kaptelov EYu, Pronin IP, Pronin VP. Radially oriented lateral self-polarization in spherulitic lead zirconate titanate thin films. *Technical Physics Letters.* 2023;49(11): 45–47.
18. Staritsyn MV. Anormalous electron channeling in PZT thin films. *Condensed Matter and Interfaces.* 2023;25(4): 572–580.
19. Jaffe B, Cook W, Jaffe H. *Piezoelectric Ceramics*. London: Academic Press; 1971.
20. Xu Y. *Ferroelectric materials and their applications*. Amsterdam: North Holland; 1991.
21. Izyumskaya N, Alivov YI, Cho SJ, Morkoç H, Lee H, Kang YS. Processing, structure, properties, and applications of PZT thin films. *Critical Reviews in Solid State and Materials Sciences.* 2007;32: 111–202.
22. Balke N, Bdikin I, Kalinin SV, Kholkin AL. Electromechanical imaging and spectroscopy of ferroelectric and piezoelectric materials: state of the art and prospects for the future. *Journal of American Ceramic Society.* 2009;92(8): 1629–1647.
23. Selvamani R. Vibration of a hydrostatic stressed piezoelectric layer embedded on gravitating half space with sliding interface boundary. *Materials Physics and Mechanics.* 2020;44(2): 238–249.
24. Ma Y, Song J, Wang X, Liu Y, Zhou J. Synthesis, microstructure and properties of magnetron sputtered lead zirconate titanate (PZT) thin film. *Coatings.* 2021;11(8): 944.
25. Cox DE, Noheda B, Shirane G. Low-temperature phases in PbZr0.52Ti0.48O3: A neutron powder diffraction study. *Physics Review B.* 2005;71(13): 134110.
26. Cordero F. Elastic properties and enhanced piezoelectric response at morphotropic phase boundaries. *Materials.* 2015; 8(12): 8195–8245.
27. Reznichenko LA, Shilkina LA, Razumovskaya ON, Yaroslavtseva EA, Dudkina SI, Demchenko OA, Yurasov YuI, Esis AA, Andryushina IN. Phase formation in near-morphotropic region of the PbZr1−xTixO3 system, structural defects, and electromechanical properties of the solid solutions. *Physics of the Solid State.* 2009;51: 1010–1018.
28. Bruchhaus R, Pitzer D, Schreiter M, Wersing W. Optimized PZT thin films for pyroelectric IR detector arrays. *Journal of Electroceramics.* 1999;3(2): 151–162.
29. Pronin IP, Kaptelov EYu, Gol'tsev AV, Afanasjev VP. The effect of stresses on self-polarization of thin ferroelectric films. *Solid State Physics.* 2003;45(9): 1768–1773.
30. Pertsev NA, Kukhar VG, Kohlstedt H, Waser R. Phase diagrams and physical properties of single-domain epitaxial Pb(Zr1−xTix)O3 thin films. *Physical Review B.* 2003;67(5): 054107.

31. Pronin VP, Dolgintsev DM, Osipov VV, Pronin IP, Senkevich SV, Kaptelov EYu. The change in the phase state of thin PZT layers in the region of the morphotropic phase boundary obtained by the RF magnetron sputtering with varying target-substrate distance. 25th International Conference on Vacuum Technique and Technology. *IOP Conf. Series: Materials Science and Engineering.* 2018; 387(1): 012063.
32. Nazeer H, Nguyen MD, Sukas ÖS, Rijnders G, Abelmann L, Elwenspoek MC. Compositional dependence of the Young's modulus and piezoelectric coefficient of (110)-oriented pulsed laser deposited PZT thin films. *Journal of Microelectromechanical Systems.* 2015;24(1): 166–173.
33. Yagnamurthy S, Chasiotis I, Lambros J, Polcawich RG, Pulskamp JS, Dubey M. Mechanical and ferroelectric behavior of PZT-based thin films. *Journal of Microelectromechanical Systems.* 2011;20(6): 1250–1258.
34. Sheen D, Kim J-J. Dielectric and polarization switching anomalies near the morphotropic phase boundary in Pb(Zr1–xTix)O3 ferroelectric thin films. *Physical Review B.* 2003;67(14): 144102.

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