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Features of electronic images of spherulitic islands in thin PZT films

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In thin films of lead zirconate titanate (PZT), obtained by two-stage radio-frequency magnetron sputtering, unusual electronic images were discovered — Kikuchi channeling lines obtained in the backscattered electron mode. The reasons for the appearance of such images in spherulitic crystals are discussed..

Keywords: thin films of lead zirconate titanate, spherulitic microstructure, scanning electron microscopy, Kikuchi channeling lines.

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The growing interest in radial-radiant-type spherulitic structures observed recently is related to attempts to get to a better understanding of the nature of crystallization of both bulk and thin-film polycrystalline compounds, to identify the features of their physical properties, and to evaluate the possibilities of their practical use [1–12]. A distinctive feature of the microstructure of such spherulites in thin films is the rotation of the crystal lattice during their growth, because of which they were named „rotational" crystals. As it turned out, such structures are very common among various oxides: in hematite [3], quartz [5,6], copper oxide [7], ferroelectrics [4,8,9], indium oxide [10] and in many other compounds. The gradient of lattice tilting in them differs by more than two orders of magnitude: from fractions of deg/μm in quartz to more than a hundred deg/μm in hematite [3,5,6]. Studies show that the nature of radial-radiant structures can vary greatly [3,5–13]. Images of one such structure, obtained in the mode of back-scattered electrons, were recorded in spherulitic islands during crystallization from the amorphous phase of nanometer semiconductor layers of indium oxide with the addition of silicon dioxide (InSiO films) and interpreted as a set of Kikuchi [10] lines. The authors attribute the possibility of observing Kikuchi lines not only to the fact that the spherulitic islands were rotational crystals in which the crystal lattice rotated in radial directions (with the magnitude of the gradient ~ 20 deg/μm) but also to the azimuthal homogeneity of this reversal. In the opposite case (e.g., in the presence of a radial-radiant structure and a difference in the rate of tilting from ray to ray), no Kikuchi images were observed. Note that previously undecipherable images were observed not only in spherulitic islands in InSiO films, but also in single-phase lead zirconate titanate (PZT) [11,13] films. The practical interest in PZT thin films is due to their rapidly growing use in microelectromechanics as well as in a number of other applications [14,15]. The detection of Kikuchi channeling in InSiO films allowed us to start focused studies of the effect in PZT thin films [16].

The aim of the present work is to study the microstructure features of spherulite islands in PZT thin films, leading to the possibility of observing Kikuchi lines.

PZT spherulite islands were formed by a two-step method of high-frequency magnetron deposition on platinized substrates of ST-50 [11] glass ceramic. The thickness of the PZT layer was ~ 900 nm. The composition of the atomized ceramic target corresponded to the elemental ratio of Zr/Ti = 54/46. The annealing of the deposited amorphous films was carried out at the temperature of 530 °C for one hour, which allowed to obtain a two-phase structure in the form of individual perovskite islands with diametric dimensions within $30-40\,\mu$m surrounded by a matrix of low-temperature pyrochlore phase.

A Tescan Lyra 3 scanning electron microscope equipped with an attachment for recording backscattered electron diffraction patterns was used to obtain electron images of the spherulitic islands. Processing of diffraction patterns allows us to generate point-by-point orientation maps of spherulitic islands with data on crystal-lattice orientation and, on their basis, to construct maps of the distribution of disorientation angles within each island with respect to a certain average position (grain reference orientation deviation, GROD), which was usually the centers of the islands.

Fig. 1, *a* shows an image of a spherulitic island obtained in the backscattered electron mode. The incident beam energy was 12 keV, and the divergence angle was no more than 0.15 deg. The obtained image in the form of intersecting bands resembling the diffraction patterns of Kikuchi [17] is fundamentally different from the previously

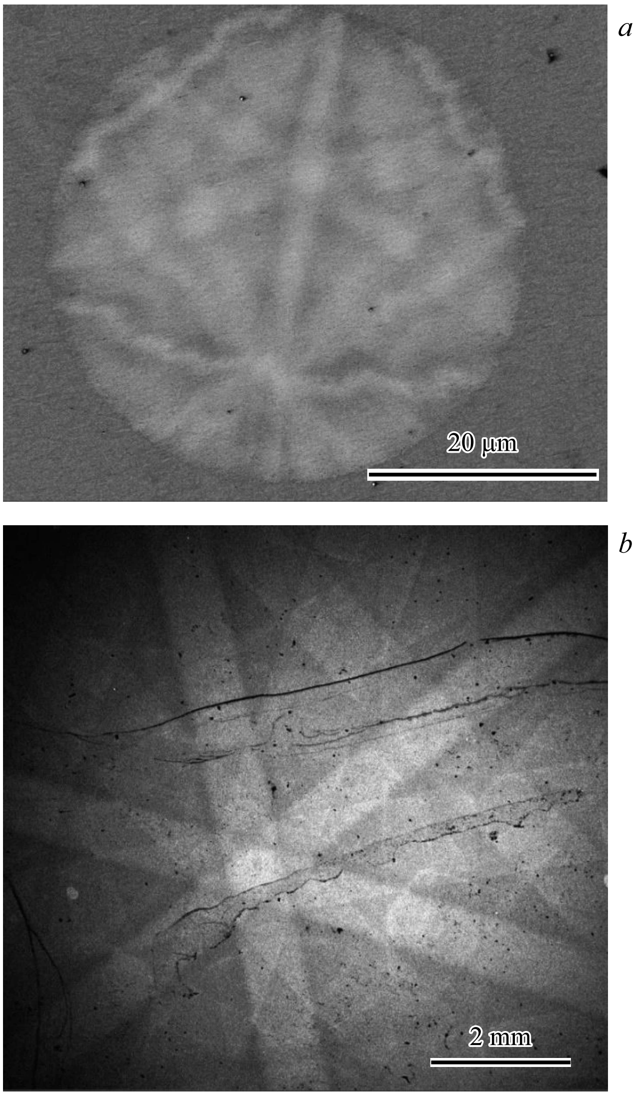

Figure 1. The electron channeling patterns of the PZT island formed on a glass ceramic substrate (*a*) and a silicon single crystal (*b*) observed in a scanning electron microscope.

studied electron images of spherulitic islands in thin PZT films characterized by a radial-radiant structure [12,13,18], and also differs markedly from the Kikuchi patterns found in InSiO [10] films. To compare, Fig. 1, *b* shows the electron channeling pattern [16] of a silicon single crystal when scanned by an electron beam at a solid angle of 30 deg, which is similar to that observed on a spherulitic PZT island.

Fig. 2, *a* shows the GROD image of the island, indicating azimuthal-uniform lattice reversal in agreement with the results of [10]. The dependence of the rotational angle on the radius of the island was close to linear (Fig. 2, *b*). The rotational gradient was $\sim 1.4-1.5$ deg/μm, which is on average $1.5-2$ times higher than in spherulites with radial-radiant microstructure [13]. Apparently, this is due to the relaxation of mechanical stresses at the ray boundaries.

Fig. 2, *c* shows a schematic model of the crystal lattice rotation due to the sequential formation of edge dislocations caused by the action of two-dimensional tensile mechanical stresses in the plane of the thin film. In some studies, the causes of mechanical stresses in thin films formed on massive substrates are attributed to the formation of a crystalline (denser) phase from an amorphous (less dense) phase as a result of high-temperature annealing [3–13]. In our case, mechanical stresses can reach values exceeding the elasticity limit due to the difference in density between the perovskite and pyrochlore phases, reaching 8 %. Therefore, as a rule, crystallization of the perovskite phase is realized in two stages (through the „porous" perovskite phase) [19].

By applying the indexing algorithms for Kikuchi diffraction patterns, we can also index the channeling patterns by matching the bands in the patterns to the lattice planes under the assumption of quasi-cubic symmetry of the perovskite lattice. The Miller indexes of these planes are shown in Fig. 3, where the lattice orientations for some of the nodal zones of the picture, which are matched to the channeling picture, are also shown. Unlike the channeling patterns obtained on the InSiO [10] thin film, in the spherulitic PZT islands one can observe a set of crystallographic directions and nodes of their intersection, by which one can judge the orientation of the thin film relative to the substrate plane. This is due both to the relatively large transverse dimensions of the islands (several tens of micrometers in diameter) and to the orientation correlation in the substrate plane of perovskite grains, the transverse size of which varies in the range $50-150$ nm [20]. It can also be assumed that the appearance of spherulitic structures exhibiting channeling patterns is also favored by the low roughness of the thin films.

Thus, in two-phase PZT thin films consisting of spherulitic islands of perovskite phase surrounded by a matrix of low-temperature phase, Kikuchi electron channeling can be observed under the condition of orientational correlation of perovskite grains in the film plane, which leads to the formation of a more ordered crystal structure, in particular depending on the degree of roughness of the lower platinum electrode. In this case, the crystal lattice undergoes azimuth-uniform rotation as the islet grows radially and is characterized by a higher rotational rate than in similar radial-radiant spherulites. Analysis of Kikuchi channeling patterns provides reliable information on the orientation and crystal lattice deformation of the spherulitic lattice structure of thin PZT films.

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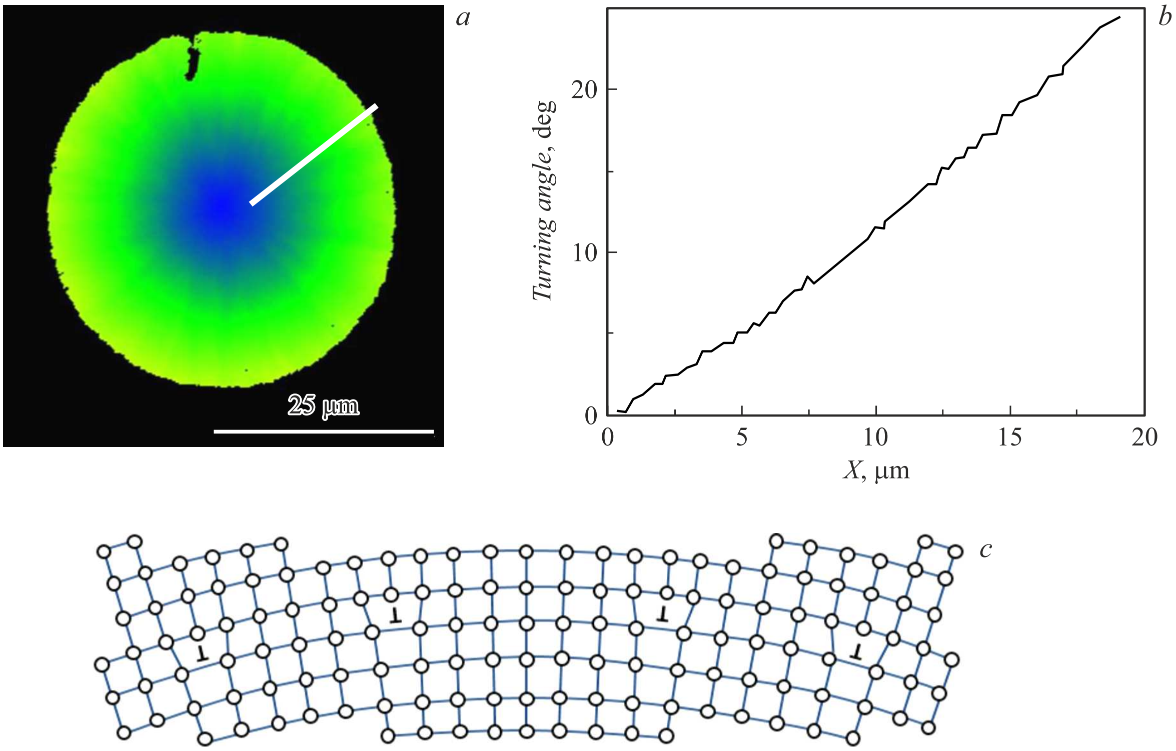

Figure 2. *a* — GROD map of the spherulite; *b* — profile of the dependence of the lattice orientation angle on the radius of the spherulitic island; *c* — model of the lattice rotation of the block along the radial directions.

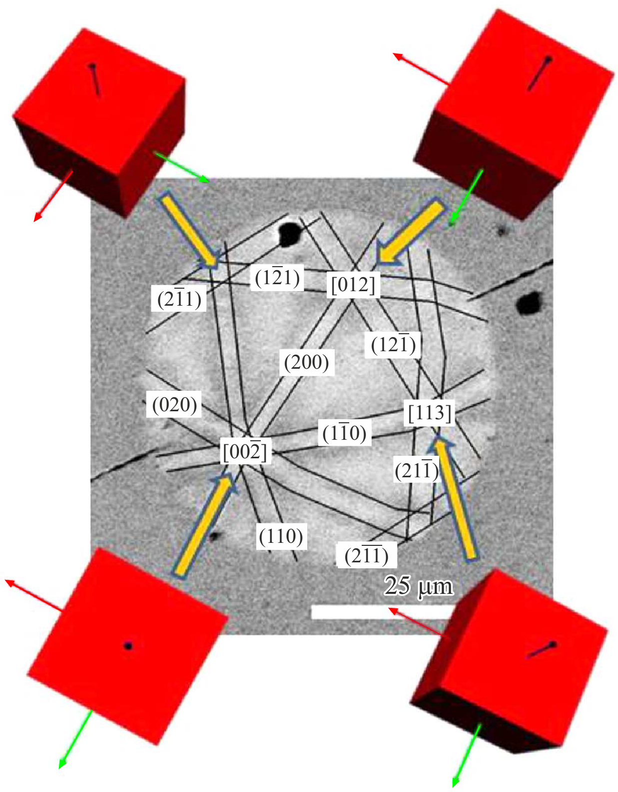

Figure 3. Image of the electron channeling pattern with superimposed indexing of the positions of lattice planes and directions.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] A.G. Shtukenberg, Yu.O. Punin, E. Gunn, B. Kahr, Chem. Rev., **112** (3), 1805 (2012). DOI: 10.1021/cr200297f

[2] A.G. Shtukenberg, Yu.O. Punin, A. Gujral, B. Kahr, Angew. Chem., **53** (3), 672 (2014). DOI: 10.1002/anie.201301223

[3] V.Yu. Kolosov, A.R. Thölén, Acta Mater., **48** (8), 1829 (2000). DOI: 10.1016/S1359-6454(99)00471-1

[4] O.M. Zhigalina, D.N. Khmelenin, Yu.A. Valieva, V.Yu. Kolosov, A.O. Bokunyaeva, G.B. Kuznetsov, K.A. Vorotilov, A.S. Sigov, Cryst. Rep., **63** (4), 646 (2018). DOI: 10.1134/S1063774518040314

[5] L. Gránásy, T. Pusztai, G. Tegze, J.A. Warren, J.F. Douglas, Phys. Rev. E, **72** (1), 011605 (2005). DOI: 10.1103/PhysRevE.72.011605].

[6] V.Yu. Kolosov, L.M. Veretennikov, Yu.B. Startseva, C.L. Schvamm, Semiconductors, **39** (8), 955 (2005). DOI: 10.1134/1.2010692

[7] N.R. Lutjes, S. Zhou, J. Antoja-Lleonart, B. Noheda, V. Ocelík, Sci. Rep., **11**, 14888 (2021). DOI: 10.1038/s41598-021-94147-y

[8] E.J. Musterman, V. Dierolf, H. Jain, Int. J. Appl. Glass Sci., **13** (3), 402 (2022). DOI: 10.1111/ijag.16574

[9] W. Sun, W. Zhou, RSC Adv., **12**, 20022 (2022). DOI: 10.1039/D2RA03302J

[10] B. Da, L. Cheng, X. Liu, K. Shigeto, K. Tsukagoshi, T. Nabatame, Z. Ding, Y. Sun, J. Hu, J. Liu, D. Tang, H. Zhang, Z. Gao, H. Guo, H. Yoshikawa, S. Tanuma, Sci. Technol. Adv. Mater. Meth., **3** (1), 2230870 (2023). DOI: 10.1080/27660400.2023.2230870

[11] E.M. Alkoy, S. Alkoy, T. Shiosaki, Ceram. Int., **33** (8), 1455 (2007). DOI: 10.1016/j.ceramint.2006.06.010

[12] D.A. Kiselev, M.V. Staritsyn, S.V. Senkevich, E.Yu. Kaptelov, I.P. Pronin, V.P. Pronin, Tech. Phys. Lett., **49** (11), 45 (2023). DOI: 10.61011/TPL.2023.11.57198.19700.

[13] M.V. Staritsyn, D.A. Kiselev, V.P. Pronin, A.N. Krushelnitsky, S.V. Senkevich, E.Yu. Kaptelov, I.P. Pronin, Phys.-chim. aspekty izucheniya klasterov, nano-strukturas i nano-materialov, vyp. **15**, 196 (2023). (in Russian) DOI: 10.26456/pcascnn/2023.15.196

[14] L. Song, S. Glinsek, E. Defay, Appl. Phys. Rev., **8** (4), 041315 (2021). DOI: 10.1063/5.0054004

[15] Y. Ma, J. Song, X. Wang, Y. Liu, J. Zhou, Coatings, **11** (8), 944 (2021). DOI: 10.3390/coatings11080944

[16] M.V. Staritsyn, Kondensirovannye sredy i mezhfaznye granitsy, **25** (4), 572 (2023) (in Russian). DOI: 10.17308/kcmf.2023.25/11481

[17] J.I. Goldstein, D.E. Newbury, J.R. Michael, N.W.M. Ritchie, J.H.J. Scott, D.C. Joy, *Scanning electron microscopy and X-ray microanalysis* (Springer, N.Y., 2018). DOI: 10.1007/978-1-4939-6676-9

[18] A.S. Elshin, I.P. Pronin, S.V. Senkevich, E.D. Mishina, Tech. Phys. Lett., **46** (4), 385 (2020). DOI: 10.1134/S1063785020040215

[19] I.P. Pronin, E.Yu. Kaptelov, S.A. Senkevich, V.A. Klimov, N.V. Zaitseva, T.A. Shaplygina, V.P. Pronin, S.A. Kukushkin, Phys. Solid State, **52** (1), 132 (2010). DOI: 10.1134/S1063783410010233

[20] V.P. Afanasjev, G.N. Mosina, A.A. Petrov, I.P. Pronin, L.M. Sorokin, E.A. Tarakanov, Tech. Phys. Lett., **27** (6), 467 (2001). DOI: 10.1134/1.1383827

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