06,07

Hysteresis and relaxation of inhomogeneous strain under converse flexoelectric effect in $SrTiO_3$ single crystal thin plates

© V.G. Zalessky, E.D. Obozova, P.P. Syrnikov

Ioffe Institute,
St. Petersburg, Russia

E-mail: nsh@mail.ioffe.ru

Received June 5, 2024
Revised June 5, 2024
Accepted June 12, 2024

The quasi-stationary converse flexoelectric effect in $SrTiO_3$ single crystal thin plates has been studied and flexoelectric coefficients have been estimated. Induced inhomogeneous strain accompanied by hysteresis and relaxation processes have been investigated.

Keywords: Flexoelectric effect, Strontium Titanate, Ferroelectrics, Elasticity, Relaxation.

DOI: 10.61011/PSS.2024.08.59057.155

1. Introduction

During last two decades the flexoelectric effect attracted the attention of specialists in the field of integrated electronics and the design of new generation microelectromechanical systems [1–5]. The interest is due to the fact that this electromechanical effect becomes significant in semiconductor and dielectric objects of submicron and nanoscopic size. The phenomenon is based on mutual relationship between dielectric polarization and strain gradient which is characterized by the flexoelectric tensor of fourth rank [1,2]:

$$P_i = \mu_{klij} \frac{\partial u_{kl}}{\partial x_j}. \quad (1)$$

Like piezoelectricity, the flexoelectricity is divided into direct and converse effects. In case of direct effect the inhomogeneous strain of crystals of finite dimensions induces the dielectric polarization, and the converse effect is associated with occurrence of inhomogeneous deformation during polarization in the external electric field [1,2]. In the phenomenological theory of flexoelectricity these phenomena are described by a system of two electromechanical equations [1]:

$$E_i = \chi_{ij}^{-1} P_j - f_{klij} \frac{\partial u_{kl}}{\partial x_j}, \quad (2a)$$

$$\sigma_{ij} = c_{ijkl} u_{kl} + f_{ijkl} \frac{\partial P_k}{\partial x_l}, \quad (2b)$$

where, E_i — electric field, χ_{ij} — dielectric susceptibility, P_j — polarization, $f_{klij} = \mu_{klij}/\chi_{ij}$ — tensor of flexoelectrical interaction, u_{kl} — strain, c_{ijkl} — elasticity factor. Further indices will be used in Vogt designation: $c_{1111} = c_{11}$, $\mu_{1133} = \mu_{13}$ etc.

The flexoelectric coefficients are directly proportional to polarizability of dielectric, so the flexoelectric effect is most pronounced in materials with high dielectric susceptibility, for example, in ferroelectrics and related materials [1,2]. To study flexoelectricity the crystals $SrTiO_3$ (hereinafter — ST) are the most convenient, as they have the maximum dielectric permittivity ($\varepsilon \approx 300$ at $T = 300$ K), and cubic symmetry of the crystal structure (O_h^1) excludes piezoelectricity, which can mask the flexoelectric response. For ST crystals the flexoelectric coefficients were measured: $\mu_{11} = 0.2$, $\mu_{12} = 7$ when studying the direct effect [6] and $\mu_{12} = 4.2$ nC/m during converse effect [7]. These experimental measured values are in good agreement with theoretical calculations from first principles: $\mu_{11} = -0.26$ and $\mu_{12} = -3.75$ nC/m [8]. But there are publications stating significant difference of measured and calculated coefficients, up to several orders of magnitude. For example, in paper [9] studying quasi-stationary converse flexoelectric effect the value of effective transverse coefficient $\tilde{\mu}_{12} \approx 4.5\,\mu$C/m was obtained. In another experiment [10] application of high voltage to planar electrodes caused non-uniform deformation due to converse flexoelectric effect, when, according to made estimations, the coefficient $\tilde{\mu}_{12}$ achieved value 6.334 mC/m. We can suppose that reason of such significant differences is due to the experiment conditions, such as: frequency dependence of flexoelectric response on external mechanical or electrical field, hysteresis and relaxation processes, and geometry and mechanical properties of samples.

Our preliminary interferometry measurements of static converse effect determined the hysteresis of „nonferroelectric“ nature in single-crystals ST [9,11]. The hysteresis is characterized by threshold electric field and residual deformation after voltage switch off. This phenomenon also made in difficult to determine the type of inhomogeneous deformation (cylindrical and spherical bends) due to significant scattering of experimental points on profiles of cross-sections of thin plates. So, the present paper target is more detail study of flexoelectric hysteresis in ST-single crystals.

2. Experiment

Samples were high quality ST-single crystal plates 140 μm thick and with area of work surface (001) $12 \times 12\,\text{mm}^2$. Gold electrodes with diameter 10 mm and thickness 25 nm were deposited on optically polished surfaces by method of thermal sputtering. The electrodes also served as mirrors for measuring local strains using an optical interferometer-microscope with an accuracy of up to 10 nm [12]. Plates were secured at edges along fixed contour with diameter 11 mm (Spherical Banding Method, SpB method) (Figure 1). The experimental set-up ensured measurement of plate surface deflection δZ, as response to external electric field and external heterogeneous mechanical stress (Figure 1, *a* and *b*, respectively). To measure hysteresis of induced strain the triangular pulses of different polarity with amplitude up to ± 750 V ($E = \pm 55$ kV/cm) and duration 15 s were applied to electrodes. In second part of experiment we studied the slow strain response when external electric field with duration up to 2 min is switched on, and strain relaxation after field switching off. Additionally strain of spherical bend was studied, it was created by needle sapphire probe with radius of curvature 0.1 mm with static load $F = 0.5$ N, directed to center of plate surface (Figure 1, *b*).

Figure 2 shows field dependence of surface deflection of plate $\delta Z(E)$, induced by triangular pulses of voltage with duration 15 s and different polarity (Figure 2, insert). The concave surface is observed from the side of the positively charged electrode. Dark and white dots on Figure correspond to surface bends in two perpendicular directions. Coincidence or divergence of dark and white dots means spherical or cylindrical bend, respectively [12]. The field dependence of strain $\delta Z(E)$ has hysteresis nature: strain starts when threshold field achieves value $E_{\text{th}} = 35$ kV/cm, further bend linearly increases with field increasing. Field decreasing is accompanied by decrease in strain with some time delay, and after field switching off the residual strain δZ_{rem} is observed.

The nature of hysteresis appears to be relaxational. To measure parameters of process of strain setting and relaxation the voltage pulses were used in form of trapezoid, they comprise linear increasing with rate 50 V/s, voltage stabilization at level 750 V ($E = \pm 55$ kV/cm) for 1−2 min and instantaneous disconnection (Figure 3). The Figure shows that at initial state the strain increases linearly with increase in field, and this increasing does not depend on the polarity. In stationary field the strain gradually increases with plateau achievement, at that strain value of negatively charged plate surface is noticeably higher then in case of surface with positive polarity. The obtained experimental points can be approximated by the exponential expression for the process of induced strain establishment:

$$\delta Z(t) = \delta Z_{\max}[1 - \exp(-t/\tau_{\text{set}})], \qquad (3)$$

where $\delta Z_{\max}$ — maximum values of strain, τ_{set} — characteristic time of strain setting. In Figure 3, *b* individually plotted

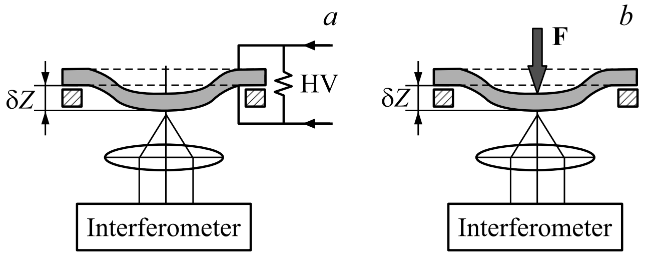

Figure 1. Diagram of set-up to study inhomogeneous strain induced: *a*) by external electric field, *b*) by local mechanical stress.

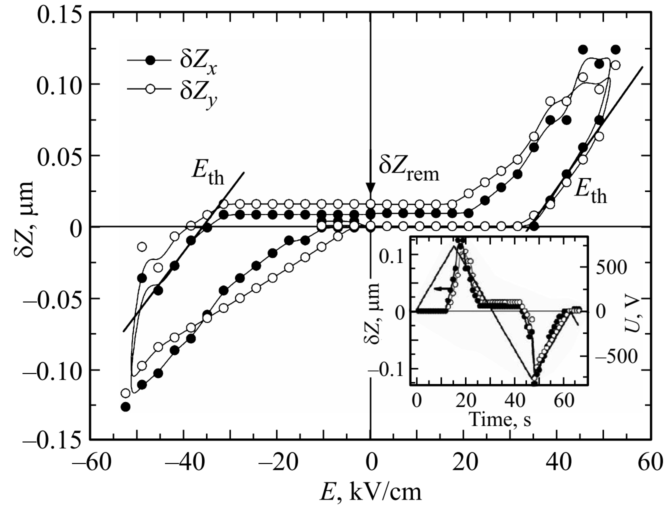

Figure 2. Deflection of ST — plates vs. external electric field. In insert — time dependence of strain as response to triangular pulses of high voltage.

in semi-logarithmic scale value $\lg(\delta Z_{\max} - \delta Z)$ vs. t ensures determination of linear sections, where the process of strain setting are well described by expression (3), and evaluation of the characteristic times $\tau_{\text{set}} = 95$ and 70 s for positive and negative polarity of the external field, respectively.

After field switching off the strain exponentially decreases to its residual value δZ_{rem}. The characteristic time of relaxation τ_{relax} can be evaluated using the following expression:

$$\delta Z(t) = \delta Z_{\max} \exp(-t/\tau_{\text{relax}}) - \delta Z_{\text{rem}}. \qquad (4)$$

By linear sections of dependence $\lg(\delta Z - \delta Z_{\text{rem}})$ vs. t the following characteristic relaxation times were obtained: $\tau_{\text{relax}} = 5 \pm 2$ and 9 ± 4 s (Figure 3, *c*). It can be seen that the relaxation times are the same for positive and negative polarities. More prolonged relaxation was not identified.

The obtained relaxation times of flexoelectric response can be compared with the relaxation of inhomogeneous deformation strain after switching off the inhomogeneous mechanical field. In stationary mode the sapphire needle probe under load 0.5 N ensured spherical bending of plate with deflection $\delta Z_{\max} = 1.2\,\mu$m. After load removal the deflection decrease, and by linear sections in dependence

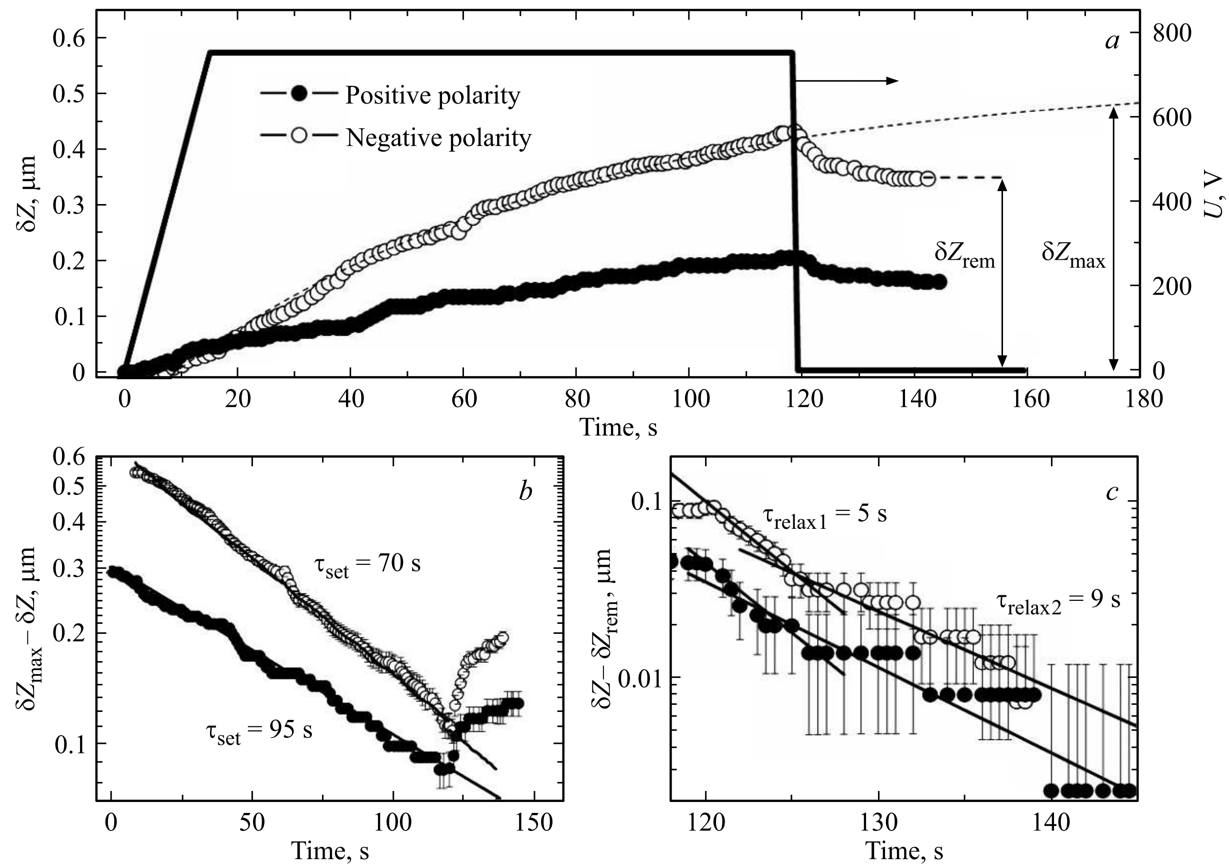

Figure 3. Deflection of plate ST, induced by long pulses of different polarity in form of trapezoid vs. time: *a*) general view, *b*) in semi-logarithmic scale for the quantity $\delta Z_{\max}-\delta Z$ for case of stationary field, *c*) semi-logarithmic scale for the quantity $(\delta Z_{\max}-\delta Z)$ after field switching off.

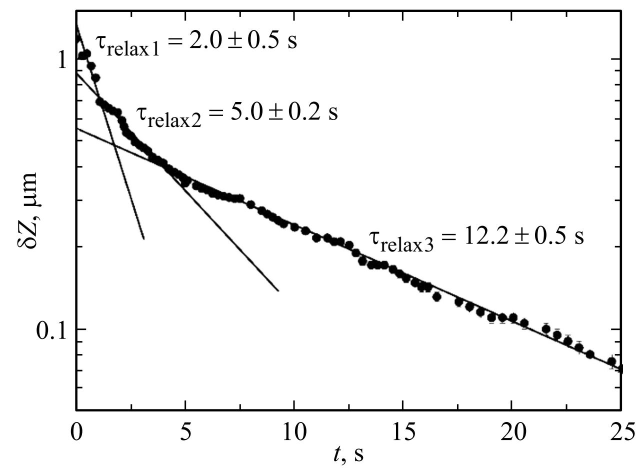

Figure 4. Relaxation of plates ST deflection after switching off inhomogeneous mechanical stress.

$\lg(\delta Z-\delta Z_{\text{rem}})$ vs. t (Figure 4) we can evaluate the characteristic relaxation times: $\tau_{\text{relax}} = 2.0 \pm 0.5$, 5.0 ± 0.2 and 12.2 ± 0.5 s. It is evident that values are rather close to the relaxation times of the flexoelectric response $\tau_{\text{relax}} = 5$ and 9 s.

3. Discussion of results

The field dependence $\delta Z(E)$ (Figure 2) ensures qualitative estimates of the effect value, in particular, effective transverse component of flexoelectric tensor $\tilde{\mu}_{12}$, using Trunov's equation [7,13]:

$$\tilde{\mu}_{12} = \frac{\sigma}{E}\,\frac{E_{\text{Y}} h^2}{12(1-\nu^2)}, \tag{5}$$

where σ — curve of surface bending, E_{Y} — Young's modulus, ν — Poison's ratio, and h — crystal thickness. Here curvature of bend can be evaluated by deflection δZ in center of plate, and by sample width d, using formula $\sigma = 8\delta Z/d^2$ [12]. If we take as ratio σ/E slope coefficient of the linear section on the dependence $\delta Z(E)$ (Figure 2) and value $E_{\text{Y}} = 2.718 \cdot 10^{11}$ Pa and $\nu = 0.238$ from data base of mechanical properties of known crystals [14], then calculation by formula (5) provides effective value of transverse flexoelectric coefficient $\tilde{\mu}_{12} \approx 3.3\,\mu$C/m. This value is combination of longitudinal and transverse coefficients

$$\tilde{\mu}_{12} = -\nu\mu_{11} + (1-\nu)\mu_{12}. \tag{6}$$

Previously, in paper [6] measurement of direct flexoelectric effect in ST plates of approximately same size provided the following values: $\mu_{11} = 0.2$, $\mu_{12} = 7\,\mathrm{nC/m}$ and their ratio $\mu_{12}/\mu_{11} = 35$. If we consider that for the converse effect the same ratio is preserved, then calculation by formula (6) provides the following values: $\mu_{11} \approx 0.12$ and $\mu_{12} \approx 4.3\,\mu\mathrm{C/m}$.

Actuality of obtained values can be checked by simple empiric calculations. First papers relating flexoelectricity presented formula $\mu \propto e/a$ (e — elementary charge, a — interatomic spacing) to evaluate flexoelectric coefficient for distorted lattice cell (see [1,2]). Papers of L. Cross's group [15,16] suggested the empiric formula of flexoelectric tensor calculation considering the dielectric susceptibility χ_{ij} and so called Scale Factor λ in as follows:

$$\mu_{klij} = \lambda \chi_{ij} \frac{e}{a}. \tag{7}$$

The Scale Factor λ depends on geometry, position state, symmetry of phases, chemical composition and technology of samples manufacturing. Scale Factor determination is subject of theoretical and experimental studies of flexoelectricity. Papers [15,16] show that for the longitudinal coefficient μ_{11} of ideal flexoelectric the Scale Factor λ shall tend to one. If empiric formula (7) is used, we obtain that for experimentally determined longitudinal flexoelectric coefficient $\mu_{11} = 0.12\,\mu\mathrm{C/m}$ and dielectric susceptibility $\chi = 300$ the Scale Factor λ is 1.0 ± 0.6, this confirms the correctness of made evaluations.

Reason of coefficient values difference as compared with other papers can be due to experiment conditions. To measure the converse effect in this work, stationary and quasi-stationary electric fields were used, whereas for the direct effect, alternating mechanical or electric fields of sufficiently high frequency served as external influences [6,7]. As under quasi-stationary conditions the polarizability of dielectrics is maximum due maximum number of different polarization mechanisms, then we can expect that flexoelectric effect will also be maximum. Besides, flexoelectric response will be accompanied by hysteresis and relaxation processes due to mechanical properties of actual crystals: finite size, elasticity and plasticity. Modeling of converse flexoelectric effect in crystals of finite size was published in [1], where expression for the induced mechanical moment bending the thin crystal plate is presented

$$M = c_{11} \int_{-h/2}^{h/2} u_{11} x_3 dx_3 - f_{13}\, h \langle P \rangle. \tag{8}$$

Here M — bending moment per unit of length, $\langle P \rangle$ — average over volume polarization, induced by external field, h — plate thickness, c_{11} — elasticity factor, u_{11} — strain tensor, f_{13} — tensor of flexoelectric interaction. Direction of coordinate x_3 corresponds to direction along plate thickness, and x_1 — direction along plate length. The first term of the equation for mechanically free plate shows that the strain response $u_{11}(x_3)$ to bending moment M depends on elasticity c_{11} and geometry of sample. Note that in case of actual crystals, during plate bending by high frequency field, the strain shall depend not only on elasticity, but on components of inertia moments determined by the sample geometry. These mechanical parameters determine the dynamics and frequency dependence of the induced strain. Example of such dynamics can be flexoelectric resonance in cantilever system based on ST — thin film [7]. Under quasi-stationary conditions the strain response $u_{11}(x_3)$ shall depend not only on elasticity, but also on plastic properties of actual crystal. In this case, when the bending moment is switched on and off, the following shall be observed: the process of bend setting, relaxation and residual deformation.

The plastic nature of relaxation of flexoelectric response in ST is confirmed by proximity of the set of characteristic relaxation times of strain $\tau_{\mathrm{relax}} = 5 \pm 2$, $9 \pm 4\,\mathrm{s}$ and $\tau_{\mathrm{relax}} = 2.0 \pm 0.5$, 5.0 ± 0.2, $12.2 \pm 0.5\,\mathrm{s}$ during electric field switching off, and after mechanical stress removal, respectively. The value of same order of magnitude $\tau_{\mathrm{relax}} = 1{-}4\,\mathrm{s}$ was obtained for polarization induced by strain gradient on same samples during study of the direct effect [17]. In the same paper the independence of this relaxation time on temperature is shown, therefore this value shall be determined purely by the mechanical properties of the crystal. It is known that ST — single crystals have unprecedented value of homogeneous plasticity among crystals of oxide compounds, reaching over 10% along axis [001], even at increasing rate of mechanical stress 10% per second [18]. Papers [19,20] showed that high plasticity of ST is due to dislocations, their sliding was initiated by oxygen vacancies.

In addition to the purely plastic nature, we can expect that the setting and relaxation of strain are associated with the spatial redistribution of charge carriers (electrons, charged vacancies and ions) in the bulk of the crystal. Mechanism of occurrence of self-consistent gradients of strain and polarization due to transport and spatial redistribution of charge carriers (electrons, charged vacancies and ions) in bulk of crystal was theoretically calculated in papers [21–23]. Self-consistent modeling of the effect showed that movement and concentration of charged defects on one side of sample can cause inhomogeneous strain due to chemical pressure or so called Vegard effect [21–23]. Besides, the hysteresis loop was forecasted in dependence of strain gradient on field strength. Feature of ST — single crystals is significant concentration of one time and two times ionized oxygen vacancies $10^{17}{-}10^{20}\,\mathrm{cm}^{-3}$, their lower formation enthalpy (about 1 eV) as compared to ions of oxygen, strontium and titanium,and high coefficients of diffusion and mobility (about $1.5 \cdot 10^{-13}\,\mathrm{cm}^2/\mathrm{V} \cdot \mathrm{s}$, in field 500 kV/cm) [24,25]. It is also known that the hysteresis on the current-voltage curve in ST during switching is associated with the transport of mobile charges consisting of dislocations, mobile oxygen ions and oxygen vacancies [26]. So, movement of oxygen vacancies from positive to negative electrode, and gradual accumulation in form of bulk charge determine the setting process. As a result the high concentration of positively charged vacancies on one side of sample near negative electrode can cause convex bend of the surface. From Figure 3 it follows that concentration of positively charged vacancies near negative electrode provides by about $1.5-2$ times higher surface strain at lower time of setting as compared to concave surface near the positive electrode. Drift, concentration and, as a result, strain response are rather slow processes. According to Figure 3, state of equilibrium of this electromechanical process can be achieved by about 70 s. We can add that such properties of hysteresis as residual deformation and threshold field are associated with the process of redistribution of positively charged vacancies when the field direction changes.

Thus, in the quasi-stationary converse flexoelectric effect, the processes of setting and relaxation of inhomogeneous strain with times greater than 2 s are caused by the crystal plasticity. The characteristic times about $1-1.5$ minutes are determined by drift and redistribution of oxygen vacancies in the external field.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] A.K. Tagantsev, P.V. Yudin. Flexoelectricity in solids: From theory to applications. World Scientific Publishing Co., Singapore (2016). 412 p.
[2] P. Zubko, G. Catalan, A. Tagantsev. Annu. Rev. Mater. Res. **43**, 387 (2013).
[3] A.A. Bukharaev, A.K. Zvezdin, A.P. Pyatakov, Yu.K. Fetisov. UFN **188**, 1288 (2018). (in Russian).
[4] W. Zhou, P. Chen, B. Chu. IET Nanodielectrics **2**, 83 (2019).
[5] B. Wang, Y. Gu, S. Zhang, L.-Q. Chen. Prog. Mater. Sci. **106**, 100570 (2019).
[6] P. Zubko, G. Catalan, A. Buckley, P.R.L. Welche, J.F. Scott. Phys. Rev. Lett. **99**, 167601 (2007). Erratum: P. Zubko, G. Catalan, A. Buckley, P.R.L. Welche, J.F. Scott. Phys. Rev. Lett. **100**, 199906 (2008).
[7] U.K. Bhaskar, N. Banerjee, A. Abdollahi, Z. Wang, D.G. Schlom, G. Rijnders, G. Catalan. Nature Nanotechnol. **11**, 263 (2015).
[8] R. Maranganti, P. Sharma. Phys. Rev. B **80**, 054109 (2009).
[9] E.D. Rumyantseva, V.G. Zalessky. FTT **56**, *7*, 1301 (2014). (in Russian).
[10] K. Wang, C. Wang, S. Huang, W. Xie, H.L. Cai, F.M. Zhang, X.S. Wu. Appl. Phys. Lett. **113**, 242903 (2018).
[11] E.D. Obozova, V.G. Zalessky. Pisma v ZTEF **103**, 792 (2016). (in Russian).
[12] E.D. Obozova, V.G. Zalessky, A.D. Polushina. Pribory i tehnika eksperimenta, **6**, 90 (2019). (in Russian).
[13] E.E.V. Bursian, N.N. Trunov. FTT **16**, 1187 (1974). (in Russian).
[14] R. Gaillac, P. Pullumbi, F.-X. Coudert. J. Phys.: Condens. Matter. **28** (2016). V. 28. P. 275201.
[15] L.E. Cross. J. Mater. Sci. **41**, *1*, 53 (2006).
[16] W. Ma, L.E. Cross. Appl. Phys. Lett. **18**, *18*, 3440 (2002).
[17] V.G. Zalessky, E.D. Obozova, A.D. Polushina, P.P. Syrnikov. FTT **63**, *10*, 1560 (2021). (in Russian).
[18] E.A. Patterson, M. Major, W. Donner, K. Durst, K.G. Webber, J. Rodel. J. Am. Ceram. Soc. **99**, *10*, 3411 (2016).
[19] W. Sigle, C. Sarbu, D. Brunner, M. Rühle. Phil. Mag. **8629**, *31*, 4809 (2006).
[20] S.-Y.Choi, S.-D. Kim, M. Choi, H.-S. Lee, J. Ryu, N. Shibata, T. Mizoguchi, E. Tochigi, T. Yamamoto, S.J. Kang, Y. Ikuhara. Nano Lett. **15**, 4129 (2015).
[21] A.N. Morozovska, E.A. Eliseev, A.K. Tagantsev, S.L. Bravina, L.-Q. Chen, S.V. Kalinin. Phys. Rev. B **83**, 195313 (2011).
[22] A.N. Morozovska, E.A. Eliseev, G.S. Svechnikov, S.V. Kalinin. Phys. Rev. B **84**, 045402 (2011).
[23] A.N. Morozovska, E.A. Eliseev, O.V. Varenyk, Y. Kim, E. Streltcov, A. Tselev, N.V. Morozovsky, S.V. Kalinin. J. Appl. Phys. **116**, 066808 (2014).
[24] W. Jiang, M. Noman, Y.M. Lu, J.A. Bain, P.A. Salvador, M. Skowronski. J. Appl. Phys. **110**, 034509 (2011).
[25] P. Pasierb, S. Komornicki, M. Rekas. J. Phys. Chem. Solids **60**, 1835 (1999).
[26] K. Szot, W. Speier, G. Bihlmayer, R. Waser. Nature Mater **5**, 312 (2006).

Translated by I.Mazurov