Bidomain Ferroelectric Crystals: Properties and Prospects of Application

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Abstract—Lithium niobate (LiNbO₃) and lithium tantalate (LiTaO₃) are among the most important and most widely used materials of coherent and nonlinear optics, as well as acoustics. The strict requirements on the uniformity and reproducibility of characteristics have become the base of the industrial technology for the production of high-quality crystals, mastered by many enterprises around the world. However, using LiNbO₃ and LiTaO₃ is not limited to the areas listed above due to their pronounced piezo and ferroelectric properties. One of the promising areas of using crystals is the creation, based on them, of electromechanical converters for precision sensors and actuators. At the same time, the high thermal stability of the piezoelectric and mechanical properties, as well as the absence of hysteresis and creep, make it possible to create electromechanical transducers capable of operating in a wide temperature range unattainable for ferroelectric materials commonly used for these purposes. The main advantage of LiNbO₃ and LiTaO₃ over other monocrystalline piezoelectrics is the possibility of a directed effect on the characteristics of devices by controlling the ferroelectric domain structure of crystals. One of the most striking examples of the use of domain engineering to create electromechanical converters based on crystals is the formation in them of the so-called bidomain structure: two macroscopic domains located in one crystal plate, having oppositely directed vectors of spontaneous polarization separated by a charged domain wall. Highly coercive switching fields make the inverse domains stable up to the Curie temperature (about 1140°C for LiNbO₃ and 600°C for LiTaO₃). This review discusses the main achievements in the field of the formation of a bidomain structure and near-surface inverse domains in LiNbO₃ and LiTaO₃ crystals. Methods for visualizing the domain structure in crystals and nondestructive methods for monitoring the position of the interdomain boundary are presented. A comparative analysis of the methods for the formation of inverse domains in crystals is carried out, and the regularities and technological methods of controlling the domain structure are discussed. The main physical models proposed in the literature to explain the effect of the formation of inverse domains are presented, and their strengths and weaknesses are considered. Methods for choosing a crystallographic cut to create devices that use bidomain crystals (BCs) are briefly listed. Examples of implementation of devices based on BCs are given: actuators, sensors, acoustic transducers, and waste energy collection systems.

Keywords: lithium niobate, lithium tantalate, bidomain crystal, diffusion annealing, crystallographic cut, actuators, sensors, magnetoelectric effect, piezoelectricity, uniaxial ferroelectric, inverse domain

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INTRODUCTION

Lithium niobate (LiNbO₃, LN) and lithium tantalate (LiTaO₃, LT) are among the most widely used oxide crystals in optics and acoustics. The unique combination of high values of nonlinear optical and piezoelectric coefficients, optical transparency in a wide wavelength range, and the possibility of directed modification of the ferroelectric domain structure have determined the importance of LN and LT in science and technology [1, 2]. The key areas of application of LN and LT are electro- and acousto-optics [3–5], holography [6, 7], generation of multiple harmonics of laser radiation [8, 9], and integrated optics [10, 11].

In recent years, however, there has been a growing interest in the application of LN and LT in mechanical-electrical converters. Monocrystallinity in combination with high piezoelectric coefficients and temperature stability allows controlled mechanical movements or small deformations to be measured with very high accuracy and reproducibility of the result. Currently, new materials for mechano-electric piezoelectric transducers are being sought. It is due to the fact that materials widely used for these purposes are based on perovskite oxide ferroelectric ceramics (for example, lead titanate-zirconate PbZr,Ti₁₋ₓO₃, PZT) with high values of piezoelectric modules have a number of disadvantages that limit their use in preci-
sion sensors and actuators. All perovskite ferroelectric ceramics are characterized by significant electromechanical hysteresis (up to 20%), creep, and the aging effect [12–17]. For the most part, these materials demonstrate a significant dependence of the piezoelectric properties on temperature and a low Curie point and, as a consequence, a narrow temperature range of applicability in the composition of devices [4]. Monocrystalline piezoelectrics, in contrast to ferroelectric ceramics, do not have these disadvantages; however, until recently, they were practically not considered for use in mechanoelectric converters due to their low (sometimes orders of magnitude lower than PZT) values of piezoelectric moduli.

The ability to control the ferroelectric domain structure of LN and LT crystals makes it possible to bypass this limitation and to increase the coefficient of conversion of the electric field into mechanical displacement due to the formation of a so-called bidomain structure in a single-crystal plate: two single-domain regions of the same volume, the vectors of spontaneous polarization of which are directed opposite to each other and are perpendicular to the interdomain border (Fig. 1). When an electric field is applied to a bidomain crystal (BC) due to the inverse piezoelectric effect, one of the domains is lengthened, while the other, which is inverted relative to the first, is shortened, which leads to the bending of the crystal plate as a whole. Thus, the BC operates similarly to a bimorph actuator, which has a serial (counter-polarized) connection of piezoelectric plates. The opposite is also true: the bending of the BC leads to the induction of charges on the surface due to the direct piezoelectric effect. Surface charges can be detected by measuring the current flowing through the external circuit when the faces or the electrical potential difference between the crystal faces are closed. The possibility of forming a bidomain structure is not unique for LN and LT (for example, the diffusion of rubidium or barium allows the formation of inverted domains in potassium titanyl phosphate (KTP) [18]). However, it is these two materials that are of greatest interest due to the combination of their high mechanoelectrical properties and temperature stability. Despite the fact that the bidomain structure is not thermodynamically in equilibrium under normal conditions due to the presence of a large charged domain wall, high domain switching fields and internal screening of the electric field originating from the charged domain wall make BCs metastable up to the Curie temperature [19].

One of the most important advantages of LN and LT crystals in comparison to lead-containing ferroelectrics and piezoceramics is the weak and linear dependence of the piezoelectric coefficients on temperature. Thus, the piezoelectric module $d_{15}$ varies for LN in the range from 50 to 470 K from 63 to 71 pC/N (≈11%); the change in the remaining coefficients is also insignificant. In the mechanical resonance mode, LN-based devices can be used at temperatures above 550°C, and the limitations imposed by an increase in electrical conductivity at such temperatures can be overcome by using the resonant frequency of the device exceeding the charge relaxation time [20].

The ability of LN and LT crystals, in the volume of which a ferroelectric bidomain structure is formed, efficiently convert the electrical potential difference into mechanical movement and vice versa in the absence of mechanoelectric hysteresis and nonlinearities can be used to create precision sensors and actuators [21]. The early brief reviews on this topic [18, 22–24] covered mainly the achievements of specific scientific groups and rather poorly described the possibilities of using a BC.

The aim of this study is to summarize the current results and prospects in the field of research and application of BC. The review is devoted to the main achievements recorded in this direction:

— the structure and properties of LN and LT crystals, which determine the possibility of forming a bidomain structure in them, are briefly discussed;

— the mechanoelectric properties of piezoelectric bimorphs and the parameters of the material necessary for the creation of effective bimorphs based on a BC were analyzed;

— prototypes of devices based on a BC, currently being manufactured and tested, and the prospects for further development of the direction for the use of crystals with a bidomain structure in devices are considered.

Fig. 1. Schematic representation of bidomain structure. The image of the thin section is taken from [19] in accordance with the CC BY 4.0 license.
Due to the fact that LN and LT are mixed oxides with a wide range of homogeneity, the properties of crystals can vary greatly depending on the composition. The most accessible crystals of a congruent composition are discussed below, unless otherwise specified.

LiNbO$_3$ and LiTaO$_3$ Crystal Structure and Methods for Determining the Direction of Spontaneous Polarization

Crystal lattices LN and LT are isomorphic to each other, at room temperature (below the Curie point) they have a pseudoilmenite structure and belong to the space symmetry group $R3c$ [1, 25, 26]. The crystallochemical structures of LN and LT are represented by the alternation of layers of oxygen atoms equidistantly located along the optical axis, forming a distorted hexagonal packing close to the densest one. The octahedral voids of the oxygen packing are occupied by Li atoms ($1/3$) and by transition metal atoms (Nb or Ta) ($1/3$), and they also remain free ($1/3$). In the direction coinciding with the vector of spontaneous polarization of the crystal $P_s$, the layers of atoms in oxygen octahedra alternate as follows [26]:

$$\ldots, \{\text{Nb(Ta), Li}\}, \{\text{Nb(Ta), Li}\}, \ldots$$

where the symbol $\Box$ denotes an empty octahedron (Fig. 2a).

The transition to the paraelectric phase LN (LT) is accompanied by a second-order phase transition of the “order-disorder” type [27, 28]. Niobium (tantalum) atoms occupy positions in the centers of oxygen octahedra, and lithium atoms acquire the ability to freely move between two adjacent octahedral voids, which on average can be considered as the location of Li in the plane of the oxygen layer separating these voids. This leads to the disappearance of spontaneous polarization and the appearance of a center of symmetry in the structure (the space symmetry group of the crystal above the Curie temperature $R3c$) (Fig. 2b).

Crystals belonging to the trigonal system can be described in terms of both a rhombohedral unit cell and a hexagonal cell. Therefore, in the literature, we can find a certain ambiguity when describing certain properties of LN and LT [29]. The complexity is also increased by the fact that a third coordinate system is used to describe the tensor properties: a rectangular Cartesian system containing 12 formula units and not coinciding with those mentioned above.

In order to avoid ambiguity, this study uses a rectangular Cartesian coordinate system in which the $x$, $y$, and $z$ axes are selected as follows:

- axis $z$ is directed along the optical axis of the crystal (direction [0001] according to Bravais in the hexagonal representation and [111] according to Miller in the rhombohedral representation), the positive direction of the axis coincides with the direction of the spontaneous polarization vector of the crystal;

- axis $x$ coincides with the direction [2TT0] by Bravais in the hexagonal representation and [$T\bar{T}$0] according to Miller in the rhombohedral representation;
—axis $y$ coincides with the direction [1 1 0 0] by Bravais in the hexagonal representation and [2 1 2] according to Miller in the rhombohedral representation.

When considering the anisotropic physical properties of crystals described by tensor quantities, the same coordinate system is used. In this case, all axes are denoted $x_n$ and the $x$ axes corresponds to index 1; axes $y$, index 2; and axes $z$, index 3 in all crystallophysical equations. This choice of axes complies with the IEEE 176-1987 standard [30]1 and allows us to unambiguously determine the crystallographic sections $x$, $y$, and $z$ (Fig. 2c).

The rest of the widely used crystallographic sections LN and LT in the overwhelming majority of cases are formed by rotating the introduced coordinate system around the $x$ axis counterclockwise by angle $\alpha$ and are denoted $y + \alpha$, and the Bravais indices of the plane corresponding to the slice can be calculated as

$$01 T - \frac{2c_{\text{hex}} \tan(\alpha)}{\sqrt{3}a_{\text{hex}}}$$

where $a_{\text{hex}}$ and $c_{\text{hex}}$ are the cell parameters in the hexagonal representation. For example, the widely used slice $y + 128^\circ$ of lithium niobate is close to the crystallographic plane with indices $(01 14)$. At the same time, the $z$-cut of the crystal in this terminology must correspond to the $y + 90^\circ$-cut (this name of the $z$-cut, however, is not used in practice for obvious reasons) [31].

To describe the methods for the formation of a bidomain ferroelectric structure in LN and LT crystals, it is also necessary to introduce the concepts of positive and negative faces (positive and negative domains in the case of a non-single-domain crystal). Let us agree in this study to call positive that face of the crystal for which the sign of the first half-wave (corresponding to the direction of the normal itself; the face for which these directions are antiparallel) will be considered negative. 1. Compression deformation along the $z$ axis leads to a displacement of cations in the direction of their positions in the centrosymmetric phase and a decrease in the dipole moment of the crystal. As a consequence, with such an impact, the positive side is charged negatively [3]. In practice, such a deformation with the simultaneous determination of the sign of the surface charge can be carried out by lightly hitting the face under study with the oscilloscope probe. In this case, the sign of the first half-wave (corresponding to the compression of the crystal) on the device display will coincide with the sign of the charge induced on the surface of the crystal and is opposite to the sign of the investigated face. In a similar way, a specially designed device can be used to determine the sign of the surface charge during crystal deformation: a piezotester.

In a BC, contrary surfaces of the crystal plate have the same sign and demonstrate the same piezoelectric response upon deformation if one of the domains is not near-surface; i.e., the depth of the interdomain boundary is not too small. Otherwise, when the inverse domain is formed in a thin near-surface region, the position of the interdomain boundary can be estimated from the frequency dependences of the crystal impedance by the method proposed in [32, 33].

The method for analyzing the frequency dependences of the impedance is as follows: upon excitation by an alternating electric signal in a single-domain plate of thickness vibrations, there are no overtones of even orders in the impedance spectra, while in the presence of a second domain, even overtones can be excited (Fig. 3a). If the boundary is at distance $\Delta$ from one of the crystal faces with thickness $t$ (for the calculation, the smaller of the distances is used), then the coefficient $k_n$ of electromechanical coupling (CEMS) of the $n$th even harmonic of the thickness vibration depends on thickness $\Delta$ of the smallest of the domains as

$$k_n(\Delta, k_r) = \frac{\sqrt{f_{n,fr}^2 - f_{n,a,n}^2}}{f_{n,a,n}} = \sqrt{2k_r} \left[ \frac{n\pi}{\Delta} + \cos(n\pi) - 2\cos(n\pi) \right], \quad (1)$$

$n \in \mathbb{Z}$,

where $k_r$ is the CEMS of the thickness vibration of a single-domain crystal, similar in geometry to the studied one, at the fundamental harmonic: $f_{n,fr}$ and $f_{n,a,n}$ are the frequencies of resonance and antiresonance of the $n$th overtone. The left side of Eq. (1) can be established from the frequency dependence of the BC impedance in the region of the $n$th overtone. To calculate the right-hand side of Eq. (1), information is needed on the value of the CEMS of a single-domain crystal at the fundamental harmonic, which can be obtained by direct measurement of the impedance of the reference sample with a geometry similar to the geometry of the studied BC. Regression analysis can be used from measurements on several even overtones to reduce the error in determining value $\Delta$.

2. Heating the crystal also leads to a decrease in the dipole moment of the crystal (the only pyroelectric coefficient $p_3 < 0$ in LN and LT crystals) and, as a consequence, to the appearance of a negative charge on the positive face due to the pyroelectric effect. In practice, the sign of the surface can be determined by the direction of the current flowing through a sensitive electrometer or ammeter with short-circuited polar faces [34].

Measurement of the magnitude of the pyroelectric current flowing through the crystal when its temperature changes can be used as a nondestructive method for determining the depth of the interdomain bound-

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1 The IEEE 176-1987 standard [30] states that, for crystals of symmetry 3m, the axes must be selected in such a way that the piezoelectric modules $d_{31}$ and $d_{33}$ are positive and the $x$, $y$, and $z$ axes form a right-handed rectangular Cartesian coordinate system.
ary in a BC due to the fact that the pyroelectric currents of counter-polarized domains are subtracted. The effective current through the external circuit with a linear temperature change at a rate of $\alpha$ can be found by the formula:

$$I_p(\Delta) = \alpha \gamma S \left(1 - \frac{2\Delta}{t}\right)$$

(2)

where $\gamma$ is the effective pyroelectric coefficient in the direction perpendicular to the BC plane and $S$ is the...
area of the electrodes [35]. In the case of an ideal BC (the domains have equal volume), the pyroelectric current decreases to zero (Fig. 3b). Formula (2) does not take into account the final conductivity of the sample, and therefore cannot be used, for example, for LN and LT crystals heat-treated in a reducing environment. The final conductivity of the samples is taken into account in [36].

The main disadvantage of the pyroelectric method for estimating the depth of an interdomain boundary in a BC is the impossibility of distinguishing a regular domain structure from a chaotic one. Thus, a completely multidomain crystal or a BC with a wide multidomain region, in which the total volumes of domains of one and the other polarizations are equal, will also give a pyroelectric current close to zero when the temperature changes. This will lead to a false conclusion about the position of the interdomain boundary at an equal distance from the plate’s faces.

The methods discussed above are straightforward and easy to implement. However, they make it possible to determine only the macroscopic polarization of crystals, while for a researcher it is often more important to control the structure of the ferroelectric domains and the interdomain boundary at the microscopic and nanoscale levels. Among the wide range of methods for visualizing domains in LN and LT crystals, the most important for the BC technology are selective etching and piezoelectric force microscopy.

Among chemical etchants of LN and LT crystals, the selective effect on the domain structure is most pronounced in hydrofluoric acid, which is often diluted with nitric acid to reduce its activity, usually in the following proportion: HF : HNO3 = 1 : 2 (vol), following the pioneering work [37]. Etching of the region where the negative domain reaches the polar z-face occurs more actively than the exit of areas of the positive domain (Fig. 3c). After etching, numerous triangular hills can be observed on the crystal surface, from the shape of which it is also possible to determine the lateral directions of the x and y axes [38]. The etching rate can be controlled by changing the dilution of the solution and its temperature [35, 39]. Thus, in the express preparation of samples for optical microscopy, etching is often carried out in a boiling etchant. In contrast, in order to obtain more reproducible results when studying small domains or thin surface layers with an inverted spontaneous polarization vector, etching can be used at room temperature for a long time [40]. The selective action of hydrofluoric acid manifests itself in all polar directions of LN and LT crystals, which makes it possible to identify domains not only on faces with a nonzero projection of the optical axis to the normal. In particular, etching makes it possible to identify domains in the BC z-cut on thin cross sections, prepared perpendicular to directions +y (1 T00) and −y (100) (the latter is etched faster) [41]. It should also be noted that LT etching is much less active compared to LN, and, therefore, high-quality visualization of the domain structure often requires longer exposures in the etchant with the use of heating.

Due to the simplicity of its implementation, selective etching is used for express control of the domain structure of single crystals in the overwhelming majority of cases, although the method is destructive. A detailed study of the process of chemical etching of lithium niobate faces was carried out in [39, 42].

Selective etching is mainly used to reveal domains at least 1 μm in size, while the resolution of the force microscopy of the piezoelectric response (piezoresponse force microscopy, PFM) allows us to study the features of the domain structure down to subnanometer sizes. The PFM method was first proposed in 1992 [43] for visualizing ferroelectric domains polarized by a probe microscope cantilever in a polymer film. Today, PFM is one of the main modes (techniques) of atomic force microscopy for studying ferroelectrics and is included as an option in many commercially available probe microscopes. When examining the domain structure in the PFM mode, the cantilever is in contact with the surface. A periodic electrical signal applied to the probe causes local mechanical vibrations of the sample surface under the action of the inverse piezoelectric effect, which are transmitted to the cantilever. The analysis of cantilever displacements makes it possible to distinguish domains with different polarizations, and also, using information on the crystallographic orientation of the sample, to establish the directions of the spontaneous polarization vector in neighboring domains (Fig. 3d). Detailed information on the features of the PFM application in the study of various types of samples can be found in reviews [44, 45].

To study the domain structure in a BC using PFM, cross sections of crystals are prepared in the form of thin polished plates with a thickness of several hundred micrometers. Using an electrically conductive paste, which acts as the lower electrode, the plates are fixed in the atomic force microscope sample holder. The procedure for preparing LN and LT crystals for investigation using PFM is described in detail in [46–49].

In addition to the four listed methods, the following nondestructive methods have been applied (at the moment, in a rather limited way):

—acoustic microscopy [50] (including in combination with probe microscopy [51]);

—a number of optical techniques, including confocal Raman [52, 53] and luminescence [54] microscopy; near-field electro-optical microscopy [55]; optical coherence tomography [56], registration and analysis of the second harmonic of laser radiation generated at the domain wall (in the far-field [57] and near-field [57, 58] modes, as well as by the Vavilov–Cherenkov mechanism [59–61]); and X-ray topography [62].
Such a wide range of methods is due to the fact that the domain wall, being a two-dimensional defect, creates a region with internal mechanical stresses in the crystal, a changed refractive index of light, and an abrupt change in the crystal polarization. Since the implementation of these methods requires rather sophisticated equipment, they have become less widespread for routine studies of the domain structure (or, at least, are less generally applicable) compared to selective etching and PFM. Examples of images obtained by the last two methods are shown in Figs. 3e and 3f, respectively.

FORMATION OF A BIDOMAIN STRUCTURE IN LiNbO$_3$ AND LiTaO$_3$ CRYSTALS

The bidomain structure in LN or LT crystals is obtained by heat treatment at temperatures close to or higher than the Curie point. Depending on the method of domain formation, preliminary heat treatments and holdings in melts of weak organic acids can be used to create the required distribution of the impurity concentration or point defects in the crystal. Annealing leads to the formation in the plate of two domains with counter-directed vectors of spontaneous polarization (if the maximum temperature was above the Curie point) or to the formation of a near-surface inverse domain in a single-domain crystal (upon annealing below the Curie point). As a result, after cooling, both sides of the BC have the same sign (both positive or both negative), and the domains are either separated by a sharp boundary of the tail-to-tail or head-to-head type (according to the generally accepted terminology [48, 49]), or a polydomain transition region of finite width [46, 47]. The position and morphology of the interdomain boundary can be controlled by changing the annealing conditions.

Selective etching is most often used to control the domain structure in the manufacture of a BC. Usually, a polished section is prepared on the end part of the plate, after removing 1–2 mm of material in order to avoid misinterpretation of the experimental results due to possible edge effects. The section can be made both at right angles to the plane of the plate, and at an angle (oblique section). In the second case, the analysis of the etching pattern is simplified; however, in numerical calculations, it is necessary to make a correction for an increase in the width of the section [46].

For the formation of two or more domains in a crystal, separated by a charged domain wall of the head-to-head or tail-to-tail type, a certain force field must be present in the volume, which is a spatial gradient of some property or effect (energetic potential), capable of influencing the orientation of the spontaneous polarization vector. The most obvious type of such a force field is the electric field $\mathbf{E}$ (opposite in direction to the gradient of the electric potential $\phi(\mathbf{r})$, where $\mathbf{r}$ is a coordinate in 3D space). It should be noted that here we do not specify this force field, implying the possibility of the influence of gradients of a different kind on the domain structure of crystals. However, since the magnitude and direction of polarization are the electrical properties of the material, any force field capable of affecting the domain structure of a ferroelectric crystal can be described in terms of some equivalent electric field (internal or external).

LN and LT are uniaxial ferroelectrics; i.e., the domain structure is affected only by the projection of the force field onto the $z$ axis, which allows us to consider the processes of formation of the domain structure in the one-dimensional case. Domain switching (changing the direction of the spontaneous polarization vector $\mathbf{P}_s$) can occur only if the value of the force field exceeds a certain coercive value. At temperatures close to the Curie point or above it, the coercive field can be vanishingly small, while at room temperature the coercive field required for domain switching can reach enormous values.

The methods for the formation of a bidomain structure can be divided into two groups according to the nature of the potential distribution in the crystal. First, the force field may exceed the coercive value in a certain limited volume, and in the rest of the crystal, it may be insufficient for polarization switching. In this case, the potential of the force field at the boundary changes monotonically (Fig. 4a). Second, the force field can exceed the coercive value in almost the entire volume of the crystal, changing the direction to the opposite in a certain region. Then, in the region of the formation of the interdomain boundary, the potential of the force field has an extremum (Fig. 4b).

It is also necessary to distinguish between the formation of a bidomain structure without a transition to the paraelectric phase and with such a transition. In the first case, a domain with opposite sign (the so-called inverse domain) is formed inside the initially single-domain region. This requires fields of significant amplitude; however, the boundary between adjacent domains is distinct and continuous. In the second case, the domain structure is formed upon cooling and passing through the Curie point; i.e., all information about the previous domain structure is lost. (Here we do not take into account possible memory effects [63, 64], which are apparently related to the internal force fields of the same kind, which is responsible for the formation of the bidomain structure.) Consequently, those regions of the crystal, where the amplitude of the force field is insufficient for unambiguous “fixation” of the direction of spontaneous polarization, remain polydomain, forming an extended transition region between two macrodomains. This region, however, does not greatly impair the performance characteristics of actuators based on the BC (the largest contribution to the deformation is made by the near-surface layers).

At low temperatures, the only currently known force field capable of changing the orientation of the
spontaneous polarization vector in LN and LT crystals is the electric field. At room temperature, the strength of the switching coercive electric field in congruent LN and LT crystals is ~2 × 10⁵ V/cm [2]. Consequently, for the formation of a bidomain structure, it is necessary to create such a distribution of the electric potential in the crystal so that the field normal to the plane of the assumed interdomain boundary in one of the domains exceeds this coercive value. Such field strength can easily be obtained in thin plates by a system of electrodes connected to an external high-voltage voltage source, charging the surface using ion or electron bombardment. In addition, it can be of a pyroelectric or piezoelectric nature.

At low temperatures, the concentrations of mobile charge carriers in LN and LT crystals are extremely low, and the processes of volume screening are extremely slow. Therefore, polarization is reversed with the formation, first of all, of domain walls with a small angle of inclination relative to the polar axis (a head-to-tail domain structure) with the minimal electric field and potential energy [65]. As a consequence, all of the above methods for obtaining an electric field in a crystal exceeding the coercive field cause the growth of needle-shaped domains at low temperatures (both in polar and nonpolar crystallographic sections) [48, 66–71] and, therefore, are unsuitable for the formation of a bidomain structure.

When the crystal is heated, the strength of the switching coercive field decreases (to hundreds of V/cm in LT and units of V/cm in LN near the Curie point [64, 72]), while the concentration of the mobile charge carriers increases, and volume screening becomes more effective. Charged domain walls, the direction of the normal to which makes a small angle with the polar axis, are formed much more easily; thus, it becomes possible to form flat extended interdomain boundaries head-to-head and tail-to-tail, and the number of different kinds of force fields that can affect the domain structure increases.

An external voltage source can be used to form an electric potential distribution with an extremum in the middle plane of a crystal plate. For this, the electrothermal cell proposed in [73] can be used. At a certain small distance above and below the plate, a set of thin wire electrodes is placed with a certain period under a

![Fig. 4. Formation of a bidomain structure by the example of an electric field $E = -\frac{d}{dz} \phi(z)$ with a monotonically changing potential (a) and with a potential having an extremum (b). ($P_s$ is the vector of spontaneous polarization in the initial single-domain state; $E_c$ is the intensity of the coercive electric field).](image-url)
common electrical potential. The second electrode (grounded) is either the metal outer casing of the oven or large area metal plates outside the oven. If the wires in the first electrode are sufficiently thin, and the second electrode is at a sufficient distance, a radial distribution of the electric potential around the wire electrode is realized, and the electric field of each individual wire decreases in inverse proportion to the distance from its axis (Fig. 5a). Correct selection of the distance between the wires and their thickness allows us to obtain an extremum of the electric potential and zero electric field in a certain plane inside the crystal, as shown in Fig. 5b. The difference in potentials is applied to the electrodes during cooling through the Curie temperature.

Despite its apparent simplicity, annealing in an electrothermal cell has not been widely used for the formation of a bidomain structure for two reasons. First, a slight displacement of the electrodes relative to each other, for example, due to elongation of the wire during heating, leads to a significant change in the nature of the domain structure and the appearance of head-to-tail domain walls (Figs. 5c, 5d). Second, the high electrical conductivity of LN at temperatures in the region of the ferroelectric phase transition causes screening of the electrostatic field at a shallow depth, as a result of which the method is not applicable to thick plates (it is clear that this remark does not apply to LT with a phase transition at a temperature of about 600°C). A separate technological problem is the supply of an electric potential to an electrothermal cell: at high temperatures, the electrical conductivity of the furnace equipment increases, which leads to difficult-to-detect current leaks and the need to use complex bushings insulated with quartz or sapphire.

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**Fig. 5.** Schematic diagram of an electrothermal cell proposed for the formation of a bidomain structure (a), the distribution of the electric potential for symmetrically located (b) and displaced relative to each other (c) electrodes, as well as the domain structure formed when the electrodes are displaced (d). Images adapted from [73] with permission from Springer Nature © 2016.
Fortunately, in addition to the external electric field, the domain structure of LN and LT crystals at temperatures near the Curie point is influenced by a number of other internal and external factors, the control of which makes it possible to create BCs without using complex electrothermal cells.

Thus, during the transition from the paraelectric phase to the ferroelectric phase, the spatial temperature gradient begins to influence the domain structure. The possibility of polarization of LN crystals in an external inhomogeneous thermal field was demonstrated in the early research on LN and LT by M. Tasson et al. in experiments on measuring the polarization of crystals when the samples are displaced relative to the center of symmetry of the thermal field of the furnace [63, 74]. Initially single-domain LN plates of the z-cut 0.5 mm thick were heated 20°C above the Curie point and then cooled in the region with a spatial temperature gradient of 100°C/cm (the temperature drop across the sample was ~5°C). During the phase transition, the orientation of the spontaneous polarization vector corresponded to the presence of a positive electric potential on the crystal face with a lower temperature (i.e., \( P_z \) turned in the direction of the temperature gradient).

The phenomenon of mono- and bidomization of LN crystals in the direction of the projection of the spatial temperature gradient on the polar axis is observed when growing small crystals. Thus, in LN crystals grown in the direction of the z axis by the method of crucible-free zone melting with laser heating, the vector of spontaneous polarization in the recrystallized part of the material is oriented in the direction of the hot zone [75, 76]. In this case, the domain structure of the seed is not inherited; if the direction of spontaneous polarization in the seed does not coincide with the direction dictated by the thermal field, the edges that face the crystal rotate around the z axis by 60°. In crystals grown in the nonpolar direction \( x \), a bidomain structure is formed with a tail-to-tail interdomain boundary perpendicular to the z axis (Fig. 6). The orientation of vectors \( P \), neighboring domains from the bulk is due to the concave shape of the crystallization front with the minimum temperature in the central part of the crystal. By changing the growth conditions, it is possible to achieve a shift of the temperature minimum from the crystal axis and, as a consequence, a shift of the interdomain boundary. In bulk crystals grown by the Czochralski method, the appearance of a bidomain structure is not observed due to small temperature drops inside the boule.

The temperature gradient inside the crystal can be used to form a bidomain structure in the LN and LT plates for subsequent use in devices. One of the methods proposed in the literature for the formation of an inhomogeneous thermal field in crystals is heat treatment in a low-inertia furnace (for example, containing infrared lamps as heating elements) with good lateral homogeneity of the thermal field. The temperature distribution is controlled by changing the conditions of reflection of the infrared radiation fluxes from the upper and lower parts of the plate, as well as by the cooling rate. The bidomain structure is formed upon cooling from the paraelectric phase, and both a technological process with a monotonically varying spatial temperature distribution [77] and an extremum inside the plate can be realized [78]. The second method is easier to implement, since a sufficiently symmetric thermal field in the crystal can be formed upon sufficiently fast cooling of the plate (about 50°C/min) in the region of the phase transition temperature. It should be noted that if the temperature profile changes rather smoothly in the region of the extremum, then an extended polydomain region is formed between two macrodomains [46, 47]. Annealing in a nonuniform thermal field can be applied with equal success to the LN and LT polar cuts, and in the second case, the transition region is much narrower (Fig. 7).

Along with the inhomogeneous temperature distribution, the domain structure is affected by the concentration gradient of own components of LN and LT, as well as some impurities. Such gradients can be formed in the crystal during growth, and also created using diffusion processes carried out both above and below the Curie point.

It is known that LN and LT are mixed oxides with a wide range of homogeneity, prone to depletion in lithium oxide during heat treatment [79–83] without changing the crystal structure up to Li2O concentrations of about 45 mol % [84, 85]. An important practical consequence of this fact, in particular, is the possibility of obtaining crystals of almost any composition by the vapor transport equilibration (VTE) method (balancing the composition by mass transfer in the gas phase). This method consists in the prolonged (for hundreds of hours) annealing of crystals in close proximity (without contact) to a polycrystalline agglomerate containing lithium oxide in a concentration that differs from the concentration in the initial crystal [86, 87].

In the classical VTE method, long-term exposure of crystals at a temperature close to the melting point leads to a change in the composition of the crystal throughout the entire volume due to diffusion processes. If the exposure time is insufficient to equalize the composition, then in the near-surface regions of the crystal, due to the difference in the rates of bulk and interphase in- or out-diffusion, a concentration gradient of Li2O arises (in other words, the gradient of the Li/Nb (Li/Ta) ratio, which can influence the direction of spontaneous polarization in the crystal. This gradient can also be regarded as the concentration gradient of intrinsic point defects. This method of forming a bidomain structure can be conventionally called diffusion annealing.
Historically, the first of the methods proposed for the formation of a bidomain structure in LN and LT crystals was annealing with holding at a temperature slightly below the Curie point. In the pioneering works of N.F. Evlanova and L.N. Rashkovich (the former Soviet Union) [88, 89] and independently in the work of N. Ognishi (Japan) [90], it was shown that with such a heat treatment at an initially positive $z$-face of an LN crystal, a thin layer is formed with an inverted direction of the spontaneous polarization vector. The resulting head-to-head domain wall is parallel to the polar face of the crystal and is spaced from it at a distance determined by the time and temperature of exposure. The presence of a dependence of the character of the domain structure on the atmosphere [22, 79] and an analysis of the composition of the crystal at different distances from the surface [82, 83] allow us to conclude that the appearance of an inverse domain upon annealing below the Curie point is related to the change in the composition of the crystal in the near-surface area.

During diffusion annealing below the Curie point, the bulk of the crystal retains its initial polarization throughout the entire time of heat treatment. The domain’s inverse with respect to this polarization gradually expands together with the increase in the volume of the near-surface region with a composition gradient. This leads to a gradual displacement of the interdomain boundary deep into the crystal, up to its stationary state, which coincides with the middle plane of the plate. The minimum temperature required for the formation of an inverse domain, which can be observed after selective etching with an optical microscope, is, according to various sources, in the range from 800–900°C [90] to 1000°C [91] and, apparently, is sufficient highly dependent on the annealing atmosphere. Thus, in [79], for the complete bidomenization of the LN plate’s $z$-cut 0.5 mm thick, about 10 h of annealing at 1110°C in a mixture of argon and water vapor and 5 h of annealing in air were required, and in [92, 93], about 1 h at 1100°C.

Fig. 6. A bidomain structure formed in LN crystals grown by crucible-free zone melting with laser heating in the direction of the $x$ axis: etched surface (a) and domain structure diagram (b). Processed and reproduced based on the data in [75] with permission from Elsevier © 1986.
According to [79], the cooling rate can also affect the thickness of the inverse layer, which is easily explained by the fact that the temperature gradient in the crystal belongs to force fields capable of changing the direction of spontaneous polarization.

In the technologically important case of annealing in air when the temperature is not changing rapidly, the minimal temperature and time required for the formation of an inverted near-surface domain with a thickness of 1 μm are ~1000°C and 1 h, respectively [91] (Fig. 8).

The bidomain structure in LN crystals can also be formed by diffusion annealing at temperatures above the Curie point. In the case of LT, annealing in the paraelectric phase is the only method capable of causing any active out-diffusion of Li₂O.

With such heat treatment above the Curie point, the entire crystal is depolarized, and the morphology of the domain structure formed upon cooling is determined (in the absence of other force fields capable of affecting the direction \( \mathbf{P}_s \)) by the volumetric concentration gradient of Li₂O. Depending on the exposure time, the formed domain structure can contain two macrodomains with oppositely directed vectors of spontaneous polarization, separated by either a transition polydomain region, or a sufficiently curved boundary. The width of the transition region decreases with increasing exposure time, which makes it possible to obtain a bidomain structure in LN crystals with characteristics that are similar to those for the case of annealing in a nonuniform thermal field (Fig. 9a). In LT crystals, diffusion processes at the same temperatures occur much more slowly. This leads to the fact that the concentration gradient Li₂O, which is sufficient to change the direction of spontaneous polarization, is formed in a narrow subsurface layer, while the main part of the crystal remains multidomain (Fig. 9b). For both LN and LT, the domain structure formed upon diffusion annealing above the Curie point has a head-to-head morphology, i.e., spontaneous polarization is directed from the surface to the bulk of the crystal [94].

Compared to diffusion annealing below the Curie point, out-diffusion in the paraelectric phase occurs in LN very actively, which leads to the rapid formation of an inhomogeneous distribution of Li₂O in a sufficiently large near-surface volume even during heating. This complicates the control of the domain sizes; therefore, diffusion annealing in air above the Curie point is less convenient for the formation of thin near-surface domains inverted relative to the bulk of the crystal.

The ideas of forming a bidomain structure by annealing LN plates at temperatures slightly below the Curie point were developed in the works of K. Nakamura et al. [22, 23, 33, 79]. It was shown that the formation of an inverse domain occurs not only in \( z \)-cut crystals but also in plates \( y + 36^\circ \)-, \( y + 127.86^\circ \)-, and \( y + 163^\circ \)-cuts, which are suitable for the manufacture of bending and torsional piezoelectric transducers. At the initial stages of heat treatment, the interdomain boundary is quite even; however, upon reaching the middle of the plate, the domain wall becomes indented, and the deviation from a straight line on the etched transverse section reaches 50 μm. In some cases, prolonged annealing led to the appearance of...
two additional thin near-surface domains in the BC, which are inverted with respect to the previously formed head-to-head configuration (tetradomain structure) [79]. In contrast, in the x- and y-cut crystals, the appearance of a bidomain structure was not observed [33, 79]. Hence it follows that the formation of an inverse near-surface domain requires the presence of a nonzero projection of the concentration gradient of Li$_2$O inside the crystal in the direction of ferroelectric polarization (axis z).

By creating asymmetric conditions for out-diffusion, it is possible that the thickness of the inverse domain exceeds half the thickness of the plate. Thus, when annealing two crystals stacked together with the –z faces, the possibility of the out-diffusion of Li$_2$O from the contacting surfaces is significantly reduced. This leads to the fact that the maximum concentration of lithium oxide in the crystals is on the initially negative crystal faces, and the interdomain boundary with a sufficiently long heat treatment shifts into the bulk beyond the middle of the plate. The LiNbO$_3$ powder applied to the surface of the plate has a similar effect on the position of the interdomain boundary upon diffusion annealing below the Curie point. In this case, a large specific surface area leads to the fact that the out-diffusion of Li$_2$O from the powder occurs more actively than from a single crystal, and the partial pressure of the lithium oxide vapor increases locally, limiting the out-diffusion from the crystal [93, 96]. However, in practice, the ability of the interdomain boundary to penetrate, during annealing under asymmetric diffusion conditions, to a distance exceeding half of the plate thickness is rarely required, since the resulting domain structure is similar to the case when the thickness of the inverse domain does not have time to reach the middle of the plate. At the same time, studying the effect of asymmetry upon annealing on the resulting bidomain structure is important, since its results allow us to confirm the diffusion nature of the formed inverse domain and establish many important regularities of domain formation upon the diffusion annealing of LN and LT.

Simple diffusion annealing makes it possible to form a head-to-head bidomain structure over the entire crystal area. This is sufficient, for example, when a simple bending actuator or waste energy collection device is subsequently manufactured based on the crystal. However, the possibility of forming counter-polarized domains with a head-to-head or tail-to-tail boundary according to the given mask is also of practical interest. For example, such domains are formed to create a periodic domain structure for systems for generating multiple harmonics of laser radiation and actuators or sensors with nonstandard geometry, as well as to study the properties of charged domain walls and devices based on them [97]. To solve this problem, getter materials can be applied to the surface that activate the out-diffusion of lithium oxide and antidiffusion barriers, while impurities can also be introduced in the crystal that can affect the domain structure.

Some oxides deposited on the LN surface are capable of accelerating the diffusion of Li$_2$O from the bulk of the crystal during high-temperature heat treatment. For example, after annealing crystals with a masked silicon oxide SiO$_x$ film at 1080°C, the formation of inverted domains under the regions with the film is observed [98–100]. (Note that the paper [101] describes the situation when domain inversion during the formation of regular domain structures (RDSs) in LN occurred outside the SiO$_x$ layer; i.e., silicon oxide acted as an antidiffusion barrier. However, we were unable to find any other evidence of a similar phenomenon in the literature, and, therefore, it can be assumed that the reason for the discrepancy with the experimental data from other sources was the error in the interpretation of etching patterns in [101] or radically different experimental conditions.)

We found that Al$_2$O$_3$ oxide’s effect on the domain structure in LN crystals is similar to that of SiO$_x$. One of the indirect confirmations of the stimulated mass transfer of Li$_2$O between LN and the aforementioned oxides is also the turbidity of the quartz and sapphire equipment in the furnace in the areas that were in the immediate vicinity of the crystal during annealing. The influence of the tooling material on out-diffusion processes decreases in the case of heat treatment in a continuous gas flow [102]; however, this approach sig-
significantly complicates the technological process and requires more expensive equipment.

At the same time, magnesium oxide can be used in high-temperature annealing as an antidiffusion barrier: upon annealing, domain inversion occurs in areas where there is no MgO mask [91]. In this case, magnesium oxide itself is widely used for doping with LN as an impurity that increases the optical stability, but does not radically change the domain structure, only slightly increasing its stability in crystals with the growth (see below) of RDSs [103].

The influence of the oxides discussed above can be explained by analyzing the phases and compounds formed in Li2O–SiO2, Li2O–Al2O3, and Li2O–MgO. Thus, in the quasi-binary Li2O–SiO2 system, at temperatures below 1100°C, a number of intermediate silicates are formed, including Li4SiO4, Li8SiO6, Li2SiO3, and Li2Si2O5 (disregarding the metastable ones) [104–106]; and in the Li2O–Al2O3 system, LiAl5O8 aluminates [107, 108]. Thus, the free energy of the crystal–oxide film interface decreases stepwise with the formation of new compounds, which is also facilitated by the polycrystalline structure of the applied mask.

In contrast, in the Li2O–MgO system, a simple eutectic is observed at 1416°C, below this temperature, lithium oxide and magnesium oxide coexist as two separate phases with limited mutual solubility [109, 110]. The region of solid solutions with a crystal lattice LN at temperatures below 1150°C is limited by the concentration of MgO at ~6 at % [111]. The diffusion coefficient of magnesium DMg in LN is below the diffusion coefficient of lithium Dli by 1–2 orders of magnitude (depending on temperature; for example, at 100°C Dli ≈ 1.6 × 10–11 cm2/s [112], and DMg ≈ 8 × 10–10 cm2/s [82]). Therefore, with a sufficient thickness of the MgO film, Mg ions do not penetrate deeply into the crystal [113], forming an antidiffusion barrier on the surface during heat treatment. Moreover, doping the near-surface layers with magnesium leads to a local increase in the Curie temperature [114], i.e., to an increase in the potential barrier of domain switching, which additionally stabilizes the domain structure and prevents the local inversion of the domain structure. Taking into account the identical effect on the Curie temperature [114], the close values of the limiting solubility in the solid phase at temperatures of ~1000°C [115, 116], and a similar form of MeO–Li2O–Nb2O5 phase diagrams [110, 116, 117], it can be assumed that in the series of metals (Me = Mg, Zn, Ni, Co, Ca), forming oxides with a valence of +2, elements that can effectively suppress out-diffusion from the surface of LN and LT can also be found. This is indirectly confirmed by the fact that the deposition of thin LN films on silicon substrates with buffer layers of MgO or ZnO makes it possible to obtain structures of a higher quality than when deposited on a substrate without a buffer layer [118, 119]. Note, however, that there is also evidence that the MgO layer can also exhibit gettering properties with respect to Li2O [120], which does not allow making an unambiguous conclusion about the nature of the out-diffusion processes with the application of such masks and suggests the need for more detailed studies.

Li2O out-diffusion can be suppressed by thin films of platinum or palladium (at least at temperatures below 1000°C [121]), which can also be used to create out-diffusion masks.

It is obvious that the use of an antidiffusion barrier for the formation of a pattern of counterpolarized domains requires careful selection of the masking film’s thickness, time and temperature, since prolonged heat treatment at a high temperature, together with high mobility and a small radius of the lithium ion, will inevitably lead to gradual degradation of the mask.

Among the metals traditionally used for the formation of inverse domains in LN crystals according to the mask, we need to mention titanium separately. Historically, titanium doping of the near-surface LN layers has been used to create regions with a changed refractive index in order to obtain optical waveguides (see, for example, the work [122]) for integrated optics devices. The appearance of an inverse domain upon the annealing of crystals with a titanium film on the surface was first discovered in [123] when analyzing the etching patterns of the surface of samples annealed at temperatures from 980 to 1100°C, and it was first considered as an undesirable effect that degrades the characteristics of Ti-diffusion waveguides. It was found that holding a crystal coated with a Ti film with a thickness of only 50 nm for 5 h at temperatures ranging from 980 to 1020°C leads to partial repolarization of the +z-surface of the crystal; and at temperatures from 1030 to 1100°C, to the complete repolarization, with the thickness of the inverse layer reaching 20 μm. The effect of the formation of a near-surface inverse domain was not observed during the diffusion of titanium in the −z-surface of the LN crystal. (It was later shown that the diffusion of Ti into the negative polar face of the crystal as a whole proceeds more slowly [124] and leads to an increase in the surface density of the hills of positive microdomains in the etching patterns of the −z-face [124, 125].)

Subsequently, the views on the appearance of inverse domains during the in-diffusion of titanium as a negative phenomenon were revised. The possibility of RDSs forming in the near-surface layers of the +z-crystal faces make Ti-diffusion annealing a useful method for creating efficient devices for generating the second harmonic of laser radiation used in integrated optics devices. Thus, in works [126, 127] on RDSs with a period of ~20 μm (Fig. 10), the second harmonic was generated with a conversion efficiency of 4 to 5%/W cm2, and the possibility of reaching 95%/W cm2, and a year later.
the authors of [128] managed to experimentally achieve a conversion efficiency of 38%/ (W cm²). In this case, if it is necessary to form optical waveguides by Ti in-diffusion without forming an inverse domain, we can use the –z-face crystal [129].

Titanium atoms are able to dissolve in LN in sufficiently high concentrations (up to 20 at % at 1187°C in crystals of a congruent composition [130]) and significantly lower the Curie temperature (from 1143 to 973°C). For comparison, the out-diffusion of Li₂O to concentrations corresponding to the boundary between LiNbO₃ and the two-phase region LiNb₂O₆ + LiNbO₃ leads to a decrease in the Curie temperature to 1035°C [131]. The diffusion coefficient of titanium in LN at 1000°C is $D_{Ti} \approx 1.7 \times 10^{-12}$ cm²/s [132], which is approximately an order of magnitude lower than the diffusion coefficient of magnesium and three orders of magnitude lower than the diffusion coefficient of lithium.

The internal electric field created by the inhomogeneous distribution of titanium ions [18] and the internal stresses introduced into the crystal lattice by an impurity [125] were considered among the possible reasons for the formation of inverted domains in Ti diffusion waveguides. However, the cause of the appearance of the near-surface inverted domain in the regions containing the Ti film can also be the gettering of the near-surface layer, as is the case with SiO₂ and Al₂O₃. When annealed in air, titanium is oxidized, and the TiO₂ layer “pulls out” Li₂O from the crystal, forming a series of intermediate compounds (Li₄TiO₄, Li₃TiO₃, Li₄Ti₅O₁₂, and Li₂Ti₃O₇) in the Li₂O—TiO₂ phase diagram [133]; and the intermediate phase in the formation of these compounds is apparently a solid solution of LiNb₃O₈ in TiO₂ having a rutile structure [134, 135]. After annealing, on those areas of the crystal surface where a sufficiently thick Ti film was deposited, a yellowish layer remains, which is probably a mixture of the compounds mentioned above (Fig. 11). However, even if the film thickness does not exceed several tens of nanometers, during annealing, opposite diffusion fluxes of Li and Ti atoms can arise, which can cause the appearance of a spatial concentration gradient of Li₂O in the crystal and cause the formation of an inverse domain. The situation arises when titanium ions concentrated near the surface, on the one hand, lower the potential barrier for switching the domain structure, and on the other hand, there is a layer with a high affinity for Li₂O, causing depletion in lithium and leading to a situation similar to the case of out-diffusion annealing.

This assumption is also confirmed by the fact that the RDSs formed upon annealing with both the SiO₂ mask and with the Ti mask have the same triangular shape in cross section, as well as the ability to erase (reverse polarize) the Ti-diffusion inverted domains by prolonged VTE annealing below the Curie temperature in an atmosphere enriched with Li₂O [129]. Note also that, according to [40], the TiO₂ deposited on an LN crystal, at low temperatures (less than 950°C) and short exposures, on the contrary, is able to prevent the out-diffusion of Li₂O.

The temperatures at which the formation of an inverse domain occurs under the action of out-diffusion stimulated by a mask of a gettering impurity on the surface are sufficiently high to also cause repolarization in regions without a film due to the out-diffusion of Li₂O. To suppress the processes of out-diffusion into the surrounding gas phase, a number of methods have been proposed, which in the general case consist of changing the composition of the atmosphere upon annealing. Thus, it was found that the out-diffusion of Li₂O partially suppresses the thermal treatment of crystals in an atmosphere saturated with water vapor [136]. (However, it should be noted that
the near-surface Ti-diffusion domains formed in LN by heat treatment in humid argon tend to stick together [22]. In addition, the crystal can be placed in the immediate vicinity of an external source of lithium oxide, for example, a sample of Li$_2$O [137] or LiNbO$_3$ [126, 138, 139] powder. If a more accurate control of the composition of the near-surface region is required, two-stage annealing can be used (first, in an atmosphere of Li$_2$O then in the atmosphere O$_2$ [140]), as well as preliminary alloying of the crystal surface with an excess of lithium oxide by annealing in Li$_2$CO$_3$ powder at 600°C for several hours [141]. The listed technological methods were proposed primarily for suppressing the out-diffusion of Li$_2$O in the formation of near-surface optical waveguides; however, they can be used with equal success to control the domain structure during annealing with the formation of inverse domains according to the given pattern.

In LT, a ferroelectric phase transition is observed at ~600°C (for crystals of a congruent composition). This means that annealing with the out-diffusion of lithium oxide or in-diffusion of most impurities cannot be carried out in a technologically reasonable time if the crystal remains in the ferroelectric state. Moreover, in comparison with LN crystals, diffusion processes in LT at the same temperatures occur much more slowly, which leads to the need to increase the temperature for the implementation of out-diffusion processes.

In principle, annealing of sufficient duration in an environment with a high or low Li$_2$O content at temperatures above 1100°C allows the formation of two counter-polarized domains in the LT plate, separated by a wide polydomain region (see Fig. 9); however, the characteristics of such a BC for practical use will be low. The use of gettering masks at temperatures above 1200°C is not always possible. For example, in the range 1250–1300°C, when the diffusion coefficient of Li in LT reaches values that are optimal from a technological point of view, eutectic melting is observed at the interface (interface) of LiTaO$_3$–TiO$_2$ [142]. Therefore, there is practically no alternative to annealing the proton-substituted crystals among the diffusion methods for the formation of an inverse domain in LT crystals.

Proton substitution (or proton exchange) is one of the methods for modifying the near-surface layers of LN and LT crystals, widely used to form optical waveguides for integrated optics devices. The method consists of doping a crystal with hydrogen atoms. The method originates from the pioneering works [143–146], in which the authors discovered the topotactic transformation of LiNbO$_3$ → HNbO$_2$ and LiTaO$_3$ → HTaO$_2$ occurring during the treatment of lithium niobate and lithium tantalate in an acidic environment with the possibility of replacing a significant fraction (up to 50 at%) of the Li$^+$ ions in the LN and LT crystals into protons without changes in the crystal symmetry. Also in [143–146], the possibility of the formation, using proton substitution, of near-surface regions with a changed refractive index of light was shown.

Near-surface proton-substituted waveguides in LN and LT are usually formed by the treatment of crystals in melts of weak acids (benzoic or pyrophosphoric with the addition of various modifiers) at temperatures of ~150 to 400°C. With this treatment, the H$^+$ protons diffuse deep into the crystal, partly replacing the lithium ions and partly occupying the interstitial positions. Studies by the method of secondary emission mass spectrometry (SIMS) showed that the distribution of protons over depth after proton substitution has a pronounced stepwise character. To reduce losses in optical waveguides formed by this method, crystals are usually annealed at temperatures from 300 to 400°C [147].

Proton substitution is an exchange reaction in which not only the introduction of protons into the crystal occurs but also the release of lithium ions from it. Thus, it becomes possible to form an inhomogeneous distribution of Li$^+$ ions at temperatures much lower than the phase transition temperature, similarly to how it occurs during annealing with the out-diffusion of Li$_2$O. Moreover, in some cases, proton substitution can lead to the formation of the LiNb$_3$O$_8$ phase of lithium that is depleted relative to LN and does not exhibit any piezoelectric properties [148]. Therefore, annealing of proton-substituted crystals at temperatures close to the Curie point makes it possible to implement the conditions for the appearance of inverse domains in the subsurface layer, both in LN and LT.

Apparently, the possibility of the formation of a bidomain structure in LT crystals subjected to proton substitution was first demonstrated by K. Nakamura and H. Shimizu [149]. In their experiments, the crystals were treated in molten benzoic acid at 220°C for various times and then annealed at 590°C (about 10°C below the Curie point). The appearance of inverse domains with thicknesses up to 100 μm in the samples was independently confirmed by selective etching and impedance spectroscopy based on the appearance of even overtones of the thickness vibrations (see Eq. (1)). It was shown later that the thickness of the inverse domain in the first approximation is proportional to the proton substitution time and can exceed the thickness of the proton-substituted layer by an order of magnitude [150].

It should be noted that, upon annealing, inverted domains in proton-substituted LT crystals are formed on the initially negative face; i.e., a tail-to-tail bidomain structure is formed [149]. This distinguishes LT from LN, where an inverse domain is formed on the initially positive face (bidomain head-to-head structure), with the exception of pyroelectric low-temperature switching (see below). The formation of an inverse domain on negative faces during the annealing of proton-substituted LT crystals allows us to create complex structures with layered domain walls.
of various types, for example, by forming positive inverse domains inside negative ones obtained previously by out-diffusion annealing [94].

The mobility of the H$^+$ and Li$^+$ ions in the crystal lattice is high at temperatures of ~600°C; therefore, with slow heating or an insufficient number of protons introduced into the lattice, the diffusion profile can flatten before the internal force field induced by it exceeds the coercive value for the given temperature. Therefore, for the formation of inverse domains, the best solution is fast annealing in furnaces with infrared heating lamps. In this case, the heating time to the holding temperature can be reduced to tens of seconds, which makes it possible to reduce the blurring of the concentration profiles of H$^+$ and Li$^+$ in the near-surface layer. The minimum heating rate required for the appearance of an inverse domain is estimated for LT to be about 4°C/min [151]. It should be noted that it is the heating rate that is important; further exposure can be for tens of minutes.

Benzoic or pyrophosphoric acids are mainly used to create proton-substituted layers for the further formation of inverted domains in LN and LT. The latter has a lower partial vapor pressure and has no boiling point: it remains liquid up to 300°C (whereas for benzoic acid, it is 260°C) and decomposes with the further increase in temperature to form orthophosphoric acid [152]. The crystals are treated in molten acid for several hours. For the formation of inverse domains to become possible, the melt temperature must be at least 200°C, and the treatment time in acid must exceed several tens of minutes [150]. An increase in the duration and temperature of the proton substitution procedure makes it possible to increase the thickness of the inverse domain; however, these dependences are not linear, and when some threshold values are reached, they are saturated [153]. After proton substitution, the crystals are washed from acid residues and annealed near the phase transition temperature.

An inverse domain is formed in proton-substituted LT crystals in a certain temperature range. Annealing at temperatures below 450°C does not change the domain structure [153–155]. During heat treatment in the range of 450°C < $T$ < $T_c$, the inverse domain is thicker the higher the annealing temperature.

Exceeding the Curie point during annealing leads to the appearance of a tail-to-tail bidomain structure, which evolves in a complex way with time [156]. A short exposure (less than 10 min) above the phase transition temperature causes the formation of near-surface macrodomains separated by a wide polydomain region. An increase in the heat treatment time leads to a gradual decrease in the thickness of the macrodomains due to the near-surface region, which becomes polydomain after cooling. In the extreme case, macrodomains disappear and the structure becomes completely polydomain (Fig. 12).

![Fig. 12. Dependence of the domain structure in a proton-substituted crystal LT face-cut from the holding time at a temperature above the Curie point (640°C).](image)

Analysis of the domain structure of LT samples, proton-substituted in pyrophosphoric acid and annealed at different temperatures and holding times, showed that the inverse domain begins to grow deep into the crystal not from the surface but from the boundary between the proton-substituted layer and the volume of the crystal that has not been changed during treatment in acid [157]. At the first stage of the repolarization process, a thin inverse domain appears over the entire area of the region with proton substitution, the thickness of which increases in proportion to the square root of the exposure time. The inverse domain grows rather rapidly in the radial direction and has a semicircular cross section. After a few minutes, the growth of the inverse domain stops, and further annealing only leads to the appearance of needle-like microdomains in it [152] (Fig. 13).

Distance $\Delta$, by which the domain wall is displaced upon annealing, can be associated with a certain diffusion length and the corresponding diffusion coefficient $D$ of the domain wall:

$$\Delta = 2\sqrt{D(T)\tau} + \Delta_0;$$  \hfill (3)

$$D(T) = D_0\exp\left(\frac{-E}{k_B T}\right),$$  \hfill (4)

where $T$ is the temperature; $\tau$ is the time; $k_B$ is the Boltzmann constant; $\Delta_0$ is the thickness of the proton-substituted layer; $D_0$ is the preexponential factor; and $E$ is the activation energy. For the case of growth of an inverse domain in an LT crystal in the direction of the z axis, $D_0 = 1.28 \times 10^9$ cm$^2$/s and $E = 3$ eV, which is much higher than the analogous constants for proton
diffusion. This allows us to conclude that the appearance of an inverse domain is not directly related to the diffusion of protons upon annealing [157].

In proton-substituted LN crystals, the inverted domain appears only upon annealing above 1000°C, and the effect of proton substitution on the near-surface domain structure is most pronounced upon pulsed heating. The growth kinetics of the inverse domain is more complex than with LT, which is apparently related to the presence of simultaneous out-diffusion processes that also affect the domain structure. A short exposure (less than 10 min at 1000°C) leads to the formation of an inverse domain on the positive face of the proton-substituted LN, similarly to what occurs in the case of out-diffusion annealing. However, an increase in the annealing time leads to the formation of two additional inverted domains on both crystal faces (tetra-domain structure) [158, 159]. In this case, on the SIMS profiles of the concentrations of Li⁺ ions and H⁺ protons, a sharp decline is observed in the initially positive face, which indicates the active out-diffusion of both components (Fig. 14). Interestingly, the proton concentration profile has two maximums, approximately coinciding in depth with the position of the tail-to-tail and head-to-head interdomain boundaries [160]. In polydomain proton-substituted LN crystals, prolonged annealing leads to the formation of near-surface domains on both faces, both of which become positive after heat treatment [161, 162].

A significant advantage of proton substitution is the ability to conduct it locally through a mask. The areas of the formation of the inverse domain subsequently coincide with the areas where the windows were formed in the mask. The mask is most often applied by magnetron sputtering of a metal that does not react with the acid during proton substitution; for example, tantalum. An important feature characterizing the proton-substituted inverse domains in LT are semicircular in cross-section edges, which distinguishes them from domains in LN, whose edges are straight and inclined with respect to the crystal surface at an angle of ≈30° [98, 151]. The RDSs formed in LT crystals by proton substitution with a mask followed by annealing more efficiently convert radiation to the second harmonic than similar RDSs obtained in LN crystals by Ti diffusion annealing [98]. This is presumably due to the lower optical losses and a more vertical (with respect to the crystal surface) domain wall.

An inverse domain can also be grown by liquid-phase epitaxy on the LN surface. Thus, in [163, 164], it was shown that when using a flux of the Li₂O–V₂O₅ system, single crystal films of doped and undoped lithium niobate can be grown. In this case, thanks to the use of a flux, the temperature of the process can be lowered to 800°C; i.e., the crystallization of the film occurs in the ferroelectric phase. An interesting regularity found in the study of films grown by this method is their polarization opposite to the direction of polarization of the substrate at the +z-faces [163, 151]. In this case, in the case of homoepitaxy of undoped LN onto a substrate of nominally pure LN, the domain structure of the growing layer had the direction of spontaneous polarization coinciding with the substrate.

In addition to the formation of inverted domains in single-crystal wafers, BCs can also be cut from bulk single crystals with a periodic domain structure formed during growth or postgrowth heat treatment.
The most common method for the formation of counter-polarized RDSs in LN and LT crystals during growth is doping the melt with substances that can affect domain formation, while simultaneously creating conditions for the appearance of periodic fluctuations of the dopant concentration along the length of the grown boule, for example, by displacing the crystal rotation axis at some distance from the axis symmetry of the thermal field when grown according to the Czochralski method. This asymmetric arrangement of the crystal leads to periodic temperature fluctuations at the crystallization front and the appearance of pronounced growth bands on the surface. Since the growth occurs above the Curie point, these fluctuations by themselves are not capable of causing the appearance of a periodically polarized domain structure; however, they lead to modulation of the growth rate and inhomogeneous entry of impurities into the crystal [165]. We can use the application of a variable potential difference between the crystal and the melt, which can affect the effective distribution coefficient of the impurity [166, 167], as an alternative method for the formation of a periodic inhomogeneous distribution of impurities in a crystal.

The set of impurities that can affect the growth domain structure is quite wide and includes transition and rare-earth metals: chromium [74], neodymium [168], yttrium [165], erbium [169], ytterbium [170], dysprosium, and europium [103]. For example, the introduction into the melt of 1 wt % Y leads to the orientation of the spontaneous polarization vector in the growth bands along the direction of yttrium’s concentration gradient [171]. The period of this as-grown domain structure formed by doping LN crystals with yttrium can be up to 10 μm, and the head-to-head and tail-to-tail domain boundaries are practically perpendicular to the z direction (Fig. 16).

Another method for the formation in LN and LT of RDSs with counter-polarized domains separated by
head-to-head and tail-to-tail boundaries is post-growth thermoelectric annealing, in which the crystal is moved through a region where it is locally heated to a temperature above Curie points. In this case, a periodically sign-changing electric voltage is applied to the crystal, which makes it possible to locally polarize the domains in the region of the crystal where the paraelectric phase changes to the ferroelectric phase [172, 173]. The method makes it possible to obtain a RDS with a period of several micrometers.

Both growth and postgrowth electrothermal annealing RDSs are well suited for the generation of the second harmonic of laser radiation. At the same time, the interrelation of the morphology of the domain structure with the temperature distribution in the crystal during the formation of a RDS makes it practically impossible to obtain flat (on a macroscopic scale) domain walls in massive crystals. Therefore, BCs cut from bulk samples with RDS are usually small, which limits their application in sensors and actuators.

MODELS PROPOSED TO EXPLAIN THE FORMATION OF INVERSE DOMAINS

As mentioned above, the cause of the local inversion of domains in LN and LT crystals is the gradient of a property or action, which can be associated with some force field capable of causing a domain to switch. In this case, all the models proposed in the literature explaining the formation of the bidomain structure ultimately assume that local switching occurs due to internal electric fields of one kind or another, depending on the method of obtaining the inverse domain. The pronounced ferroelectric properties of LN and LT make it possible to induce internal electric fields by a number of different types of influences.

One of the first explanations for the formation of inverted domains under conditions of a temperature gradient and/or a concentration gradient of the composition was the pyroelectric model. According to this model, a change in temperature upon cooling causes the appearance in the crystal of a pyroelectric field directed along the spontaneous polarization vector. It is assumed that the out-diffusion of Li_{2}O and doping of the near-surface volume with impurity atoms (Ti, H) locally lower the Curie temperature and lead to the transition to the paraelectric state of the near-surface regions of the crystal. At the interface between the para- and ferroelectric phases, upon cooling, a bound pyroelectric charge arises, which is compensated by mobile carriers from the paraelectric phase, leading to the appearance of an internal electric field in it. The field from the side of the initially negative face is directed along the vector P of the ferroelectric part of the crystal and against the vector P, from the side of the initially positive face, which should cause the formation of an inverse domain and a head-to-head boundary upon cooling [79, 123, 174].

The value of the pyroelectric coefficient modulo in LN and LT crystals increases with temperature and near the phase transition point significantly exceeds the values at room temperature [175, 176], while the domain switching field, in contrast, is small. Taking into account that, at room temperature, pyroelectric fields induced by even a small change in temperature are capable of exceeding the switching field of spontaneous polarization [35, 71, 177, 178], it can be assumed that at a temperature somewhat below the Curie point, a pyroelectric field of any magnitude should certainly lead to the repolarization of the domain.

At the same time, the electrical conductivity LN near the Curie point is ~0.1 Ohm−1 cm−1 [179], which, together with the rather low mobility characteristic of oxide crystals, allows us to conclude that the concentration of free charge carriers is high. In the most conservative case (T ≈ 1000°C, charge carriers are electrons, and ionization occurs according to the interband mechanism), we can assume that the electrical conductivity is σ ~ 10−2 Ohm−1 cm−1, the concentration of free charge carriers is not less n ~ 10^{18} cm^{−3} [179], and the dielectric constant ε ~ 1000 [180], from which it follows that the Debye length L_D and the relaxation time of the internal field τ does not exceed the following values:

\[ L_D \leq \sqrt{\frac{\varepsilon_0 e k T}{n e^2}} \approx 80 \text{ nm}, \]  \[ \tau \leq \frac{\varepsilon \varepsilon_0}{\sigma} \approx 10 \text{ ns}. \]

These estimates and the analysis of their own experimental results by a number of authors [22, 181] showed that even a significant pyroelectric field is...
almost completely and quite quickly screened at a distance of about 1.1 μm (decreases by 7 orders of magnitude at a distance of 14L₁ₙ) in LN at heat treatment temperatures typical for the formation of inverted domains by diffusion.

In LT crystals, the phase transition occurs at a lower temperature, which means lower electrical conductivity (~10⁻⁶ Ohm⁻¹ cm⁻¹ [182]) and, hence, the screening rate of the electric field. Therefore, in the case of LT, the pyroelectric repolarization of the inverted domain becomes possible. However, due to the fact that diffusion annealing (with and without impurity) is not used for the formation of a bidomain structure in LT due to the need for heating to very high temperatures, and there are no data in the literature sufficient to confirm or refute this model. It should also be noted that an obvious consequence of the fact that charges of the same sign are induced on the polar faces in LN and LT upon cooling should be that the types of the formed domain structures coincide. This is refuted by experiments with proton-substituted crystals, in which a tail-to-tail domain structure is formed. In this case, the electric closure of the polar faces of LT crystals during heat treatment does not affect the character of the domain structure [24, 152], which also testifies against the pyroelectric model.

Another effect that can lead to the appearance of an internal electric field is piezoelectricity. In [166, 183], it was suggested that the out-diffusion of Li₂O or the introduction of impurity atoms lead to a change in the lattice constant in the near-surface volume and, as a consequence, to the appearance of a piezoelectric field with a nonzero projection onto the polar axis capable of causing the polarization to switch. In the simplest case of a z-cut, the difference in the lattice parameter is responsible for the appearance of the piezoelectric effect a in the volume and in the near-surface layer. Mechanical stresses caused by the lattice parameter gradient a are directed in the plane of the plate and can be estimated by formula

\[ \sigma_{11}^{\Delta a} = \frac{1}{s_{11}} \left( \frac{1}{s_{12}} \frac{\Delta a}{a} \right), \quad (7) \]

where \( s_{11} \) and \( s_{12} \) are the components of the elastic compliance matrix (see Table 1). In the simplest case of the out-diffusion of Li₂O, the lattice parameter monotonically increases with depletion in lithium and varies almost linearly with temperature [28, 184]. For both LN and LT, the slope of the dependence \( \Delta a(C_{LiO}) \) is about 0.0002 nm/at % [80]. It is known that the depletion of the near-surface region in lithium oxide proceeds quite actively and can lead to the appearance of the lithium trinitiobate phase. In this case, the difference in the lattice parameters \( \Delta a \) between the congruent composition and the boundary of the single-phase region will be about 0.0008 nm, and the mechanical stress \( \sigma_{11}^{\Delta a} \sim 300 \) MPa. Obviously, this is the upper estimate, valid only for the case of a sharp boundary between the region with the initial and changed lattice parameters, which is not realized in practice in diffusion processes (but it is realized in epitaxy). The mechanical stresses increase as \( \Delta a \) increases. For example, when alloyed with titanium, they can lead to the appearance of microcracks on the surface [185].

The domain structure of LN and LT is influenced only by the component of the electric field \( E_{3} \) directed along the third-order axis and related to the additional polarization \( P_{3} \) caused by the piezoelectric effect:

\[ E_{3} = \frac{P_{3}}{e_{33}e_{0}} = \frac{2\sigma_{11}^{\Delta a}d_{31}}{e_{33}e_{0}}, \quad (8) \]

where \( d_{31} \) is the transverse piezoelectric module (see Table 1). The estimate, according to formula (8), gives the electric field strength of ~600 V/cm for a conservative calculation with the modulus value \( d_{31} \) at room temperature (when heating, the absolute value \( d_{31} \) increases [186]). Obviously, such an electric field strength is sufficient to switch the direction of spontaneous polarization. Even a decrease in this estimate by two orders of magnitude due to the extremum of the dielectric constant in the phase transition region and a smooth change in the lattice parameter gives the values of the electric field strength that can cause the polarization of the domain structure at high temperatures, especially in layers with a reduced switching energy barrier due to doping. Formula (8) does not take into account the longitudinal piezoelectric effect described by the piezomodule \( d_{31} \), since it is believed that the bidomain structure is formed in the z-cut of the plate. In the case of crystals of other cuts or with the growth of the domain structure, the contribution of mechanical stresses in the direction of the optical axis must be additionally taken into account [183].

If the lattice parameter a increases in the near-surface layer, then mechanical compressive stresses arise, and \( \sigma_{33}^{\Delta a} \) takes positive values (as is customary when considering the piezoelectric effect [187]). In LN and LT crystals, the transverse piezoelectric module \( d_{11} < 0 \). This means that an electric field appears in the near-surface layers opposite to the vector of spontaneous polarization in the bulk of the crystal; i.e., a head-to-head domain structure should form near the positive face, and a tail-to-tail structure near the negative face. In contrast, a decrease in the crystal lattice parameter should lead to the formation of an electric field directed from the bulk to the surface and to the absence of domain formation in the layer. In this case, in the latter case, mechanical compressive stresses are experienced by the crystal layer, in which the lattice parameter remains unchanged during the heat treatment, and, therefore, domain formation should occur starting from a certain depth.
An argument in favor of the piezoelectric theory is, for example, the difference in the type of domain structure in LN and LT crystals formed upon annealing after proton substitution; according to the literature, when protons are introduced into a crystal, the hexagonal cell parameter $a$ decreases in lithium niobate [188] and increases in lithium tantalate [189]. In addition, the inverse domain in proton-substituted crystals begins to grow not from the surface but from a certain plane in the bulk of the crystal, which, according to the SIMS data, corresponds to a stepwise transition between the proton-substituted and unaltered regions of the crystal. Thus, the repolarization is caused by mechanical stresses not in the proton-substituted layer but in the unchanged volume of the crystal. Another indirect confirmation of the appearance of a piezoelectric field in the near-surface regions of crystals is the formation of microdomains on the negative LN face annealed in contact with a titanium film [124, 125]. It was shown with the help of transmission electron microscopy [190] that such microdomains are a consequence of the formation of near-surface dislocations and are apparently related to the relaxation of significant mechanical stresses. Interestingly, the lattice parameter $a$ decreases during the in-diffusion of titanium [185], which, however, does not contradict the piezoelectric model, if we take into account that Ti ions do not diffuse deeply into the crystal, but the TiO$_2$ layer is able to effectively deplete the surface volume in terms of Li (see above). The third important fact in favor of the piezoelectric model is the formation of a bidomain structure during the liquid epitaxy of Mg-doped LN films on nominally pure LN substrates. Increasing the lattice parameter $a$ upon the addition of magnesium [191] explains the formation of an inverse domain with a head-to-head interface in the case of growing a doped film and the absence of such a domain in homoeptaxy [163]. The piezoelectric field model also explains clearly the position of domain walls in regions with an abrupt change in the concentration of Cr impurities in crystals with growth domains [166].

At the same time, the piezoelectric theory predicts the appearance of a three- rather than two-domain structure, since the vector of the piezoelectric field must be directed against the vector of spontaneous polarization on both sides of the plate. Indeed, some studies reported the appearance of an additional thin inverse domain on the initially negative side of the crystal; however, this phenomenon was difficult to reproduce and manifested itself after sufficiently long exposure at a high temperature [79, 192].

Another model of domain formation, recognized by many authors, is polarization due to the volumetric electric field related to the concentration gradient of charged defects and impurity atoms. In various sources, lithium ions [63], oxygen vacancies $V_O$ [92], antistructural defects of Nb$_{Li}$ [193], and various impurity atoms [171, 181, 194] are proposed as candidates for the role of charged centers leading to the formation of an internal electric field.

In the general case, it is assumed that during out-diffusion or doping with an impurity, a spatial concentration gradient of some charged centers is formed in the surface layer $\nabla N(t, r)$, or in the one-dimensional case $\partial N/\partial z$. The concentration profile of electrically active centers changes over time, smoothing out in volume. For the case of out-diffusion from the faces of a thin plate with a thickness $t$ the following solution of the second Fick equation was obtained, which describes the concentration distribution $N(z, t)$ in the one-dimensional case [82, 193]

$$
N(z, t) = N_0 \left[ \text{erfc} \left( \frac{L + z}{2\sqrt{D\tau}} \right) + \text{erfc} \left( \frac{L - z}{2\sqrt{D\tau}} \right) \right],
$$

where $N_0$ is the concentration of centers on the surface at the end of the diffusion process; $D$ is the diffusion coefficient; and $\tau$ is the diffusion time. In formula (9), it is assumed that the out-diffusion rates of Li$_2$O with positive and negative faces are the same.

The concentration gradient of slowly diffusing charged centers leads to the appearance of an inhomogeneous distribution of the concentration of free charge carriers (electrons), the diffusion of which leads to the appearance of an internal electric field, which prevents the separation of charges. The electric field strength $E_{in}$ associated with this gradient of charged centers can be described by the formula

$$
E_{in}(z, t) = \frac{-kT}{q} \frac{1}{N} \frac{\partial N}{\partial z},
$$

where $q$ is the charge of one center. The distribution of the electric field strength, described by Eq. (10), has a symmetrical form with respect to the median plane of the plate with two extrema in the near-surface region (Fig. 17). With an increase in the heat treatment time, the concentration profile smoothens out, leading to a decrease in the height of the peaks in the distribution of the electric field strength.

Equation (10) predicts different directions of the electric field at the $+z$ and $-z$ faces. This is in good agreement with the formation of an inverse domain on only one face, which is observed in practice.

To explain the effect of doping crystals with rare-earth metals on the domain structure during crystal growth in the direction of the $z$ axis according to the Czochralski method, with a shift of the crystal rotation axis from the symmetry axis of the thermal field, the following model was proposed in [171]. According to this model, the polarization process is due to the coexistence of two internal fields in the material: the field $E_{eq}$ of the space charge related to the ambipolar diffusion of impurity Y$^{3+}$ and its compensating charges, as well as the field $E_{eq}$ equivalent to the appearance of
additional polarization due to the inhomogeneous distribution of the Y impurity and the mechanical stresses related to it. In the first approximation and isotropic consideration of the material, both of these fields are proportional to the gradient of the impurity concentration in the crystal and add up to the total internal electric field

$$E_{\text{in}} = (C_1 + C_2)\nabla C_{\text{imp}},$$

where $C_{\text{imp}}$ is the dopant concentration, and $C_1$ and $C_2$ are constants. In the stationary case, the polarization distribution inside the ferroelectric is described by the Landau–Ginzburg–Devonshire equation, which, if we neglect the higher powers of the expansion of the free energy with respect to the order parameter, in the isotropic one-dimensional case can be written as

$$a + bP_z^2 + c \frac{d^2}{dz^2} P_z = |E_{\text{in}}|,$$  \hspace{2cm} (11)

where $a$, $b$, and $c$ are constants; and $P_z$ and $|E_{\text{in}}|$ are the projections of the polarization and internal electric field on the polar axis. In the regions of the crystal where an increase in the impurity concentration is replaced by a decrease (the extremum of the concentration profile $C_{\text{imp}}(z)$), the electric field is zero, and then Eq. (11) has the solution

$$P_z = P_{z0} \tanh \left( z \frac{a}{2c} \right),$$  \hspace{2cm} (12)

where $P_{z0}$ is the spontaneous polarization away from the domain wall. Dependence (12) has a stepped form and is valid both for sharp domain walls and for diffuse polydomain transition regions (a similar expression was obtained to describe the polarization in the region of charged 180° domain walls later in [195]).

According to the experimental data, a change in the direction of polarization corresponds to a change in the sign of the impurity concentration gradient. If the extremum of the concentration profile is smooth, then $E_{\text{in}}$ is equal to zero over a sufficiently wide section of the crystal thickness, which causes fluctuations in the direction of spontaneous polarization and leads to the formation of a sawtooth boundary or a polydomain region between adjacent domains. In the case when the concentration profile has a pronounced extremum, then the direction $E_{\text{in}}$ also changes in a small area of the volume, leading to the formation of an even, charged domain wall (Fig. 18).

The thermoelectric model should be singled out separately for the case of polarization under condi-

![Fig. 17. Dependence of the projection of the strength of the internal electric field on the optical axis $E_{\text{in}}(z,t)$ in an LN plate, calculated using Eq. (10) for the case of symmetric out-diffusion. Based on data from [193] with permission from AIP Publishing © 1994.](image-url)
tions of a non-uniform temperature distribution. According to this model, the cause of the appearance of the internal electric field, leading to the polarization of the domain, is the bulk thermoelectric field related to the gradient of the concentration of the charge carriers [63, 75]. Indeed, in a more heated region, the number of free charge carriers is higher than in a less heated one, which causes a diffusion current to flow and a volume electric field appears, which prevents the separation of charges. The Seebeck coefficient $S$ in LN at a temperature of about 1000°C, according to various estimates, ranges from 0.55 mV/°C [179] to 0.8 mV/°C [75]. The electric field arising under conditions of a spatial temperature gradient is determined by $\nabla T$ as

$$E = S\nabla T. \quad (13)$$

Assuming that the maximum temperature is in the middle plane of a single-crystal plate of the $z$-cut 0.5 mm thick, we find that to achieve a field of 1 V/cm, sufficient to switch spontaneous polarization in the region of the Curie point in LN, the temperature difference between the extremum and the surface should be about 40°C, which is quite achievable when using low-inertia infrared ovens. For LT, it is difficult to make such an estimate, but it is obvious that due to the higher electric field strength required for the crystal polarization during the phase transition and, probably, the lower Seebeck coefficient, the temperature gradient required for the formation of a bidomain structure increases.

However, according to the published data, the electrical conductivity of LN at high temperatures is

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**Fig. 18.** Yttrium concentration profile (a) along section A–A, schematically shown in the etched region of a crystal (b) with growth of RDS (quoted from [196] with permission from Taylor & Francis Group © 2001), as well as a schematic illustration (c) of the correspondence distribution of yttrium concentration along the length of the LN crystal, internal electric field $|E_{ind}|$ and morphology of the domain wall (adapted from [171] with permission from AIP Publishing © 1989).
realized by negative charge carriers, and, therefore, the Seebeck coefficient should be less than zero. Then, in the practical case, when the plate faces have a temperature lower than the volume, the electric field $E$ will be directed from the volume to the faces, and the forming domain structure will be of the tail-to-tail type, which does not correspond to the available experimental results. In addition, the issue of volume screening is not resolved: the transition to the ferroelectric phase should occur faster than the compensation of the internal field by mobile charge carriers.

The models above exhibit a number of shortcomings, as a result of which none of them is accepted as generally accepted. Thus, the question of the screening of the internal electric field by free carriers at high temperatures remains open. LN and LT have a pronounced polaron conductivity, which rather quickly compensates for the internal fields related to pyro- and piezoelectricity, at temperatures of about $500^\circ$C [20].

Another drawback of the described models is the impossibility of explaining the appearance of an additional inverse domain only upon heat treatment of a sufficient duration. This phenomenon consists in the formation of a three-domain structure with the emergence of the tail of the spontaneous polarization vector on one face of the tail, and of the head on the other (Fig. 19). The formation of an additional inverse domain was observed in out-diffusion annealing [79] and experiments with titanium diffusion [192]. Both (1) domain formation in bicrystals, which, despite the fact that it occurs under asymmetric out-diffusion conditions, can also lead to the formation of a bidomain structure [197] and (2) the secondary repolarization of BCs with the formation of a tetradomain structure are interesting.

In addition, the diffusion behavior of the domain wall with an increase in the heat treatment time and the mechanism of the erosion of domains upon annealing in an atmosphere of Li$_2$O remain unclear.

It can be assumed that the formation of inverse domains is influenced by a complex of factors, each of which is predominant in certain conditions. However, it is obvious that a universal model has not yet been proposed, and its creation requires further detailed research.

**BIMORPH EQUATIONS AND SELECTION OF THE OPTIMAL CRYSTALLOGRAPHIC CUT**

The main area of the application of a BC is bimorph mechanoelectrical converters for sensors and actuators. The characteristics of such bimorphs depend, first of all, on the piezoelectric and elastomechanical properties of the crystals used and their sections. In this section, equations are given that describe the relationship between mechanical deformation and the electric field in a BC, and a brief analysis of crystallographic sections that provide the best characteristics of single-crystal bimorphs is given.

Shift $\delta$ of the free end of the bimorph fixed in the form of a cantilever on one side is described by the equation [198] under the action of an electric voltage:

$$\delta = \frac{3}{2} d_3 V_{\text{ext}} \left(\frac{l}{l}\right)^2,$$

and angle $\gamma$, to which the free end of such a bimorph is deflected, can be calculated by the formula

$$\gamma = 3 d_3 V_{\text{ext}} \frac{l}{l},$$

where $d_3$ is the value of the transverse piezoelectric modulus corresponding to the expansion-compression deformation in the direction parallel to the long side of the bimorph and perpendicular to the electric field applied to the plate ($i, j = 1, 2, 3; i \neq j$); $V_{\text{ext}}$ is the voltage applied to the crystal; $l$ is the length of the bimorph plate; and $w$ is the thickness of the bimorph plate.

From a practical point of view, it is important when an external force is applied to the free end of bimorph $F$, the amount of displacement $\delta_F$ will be

$$\delta_F = \frac{3}{2} d_3 V \left(\frac{l}{l}\right)^2 - \frac{4s_{ij}^E}{w} \left(\frac{l}{l}\right)^3 F,$$

where $s_{ij}^E$ is the diagonal coefficient of the elastic compliance matrix of the bimorph material, measured at a constant electric field and relating the mechanical stresses and mechanical deformations in a direction parallel to the long side of the bimorph; and $w$ is the width of the bimorph plate.

Equation (16) allows us to obtain a formula for an important characteristic of the bimorph of the blocking force $F_b$, and when applied to the free end, the displacement $\delta_F = 0$:

$$F_b = \frac{3}{8} d_3 V \left(\frac{l}{l}\right)^2 w.$$

It should be noted that Eqs. (14)–(17) describe static deformations clearly and become more compli-
cated in the case when the bimorph actuator must move with a nonzero frequency. The theory of the functioning of bimorphs under the action of a time-varying control signal is described in [199, 200]. Without giving cumbersome calculations, we only note that in order to increase the operating frequency range and reduce the polarization losses of the material under the action of alternating current, we need to reduce the electrical capacity of the bimorph. With a constant value of the dielectric constant of the material along the thickness of the bimorph, the appearance of an electrical potential series bimorph, fixed in the form of a cantilever on one side, causes the appearance of an electrical potential of the control electric field.

In contrast, the displacement of the free end of the series bimorph, fixed in the form of a cantilever on one side, causes the appearance of an electrical potential difference between the electrodes on the surface $V_{ind}$, which can be defined as in [201]

$$V_{ind} = \frac{d_{xyz}}{2s_{ij}^E\varepsilon_{ij}^T} \left( \frac{1}{\varepsilon_0} \right)^2,$$

(18)

where $\varepsilon_{ij}^T$ is the static dielectric constant in the direction of the electric field applied to the plate, measured under isothermal conditions and $\varepsilon_0$ is the dielectric constant of a vacuum.

The analysis of Eqs. (14)–(18) shows that to improve the characteristics of the bimorph it is necessary to choose materials for which the relation $d_{xyz}/\left(s_{ij}^E\varepsilon_{ij}^T\right) \rightarrow \max$. A similar formula describes another important characteristic of a piezoelectric material: the transverse CEMS $k_{ij} = \sqrt{d_{xyz}^2/\left(s_{ij}^E\varepsilon_{ij}^T\right)}$ characterizing the ability to convert the energy of mechanical deformation into stored electrical energy [202, 203]. This factor is important in terms of resonant applications of BCs and crystals with inverse domains, for example, devices for collecting waste vibrational energy.

Consequently, that material (or that cut of the crystal)—which has a higher transverse piezoelectric modulus, lower compliance in the direction of deformation (elongation or compression), and less repolarization losses (dielectric constant)—has the best characteristics.

In Eqs. (14)–(18), numerical indices in the matrix coefficients describing the properties of the material are deliberately not indicated. Indeed, the anisotropic nature of LN and LT single crystals leaves a lot of freedom to optimize the characteristics of bimorphs based on BCs by choosing the best crystallographic cut of plates for sensors and actuators. In this case, depending on the choice of the cut, the indices may change the required elements of the matrices describing the properties of the material.

In most works devoted to manufacturing and studying sensors and actuators based on piezoceramic bimorphs, it is customary to use the $z$ axis as the direction of electric field application, and use the $x$ axis, which corresponds to the piezoelectric coefficient $d_{33}$, as the direction of elongation (reduction) of the deformation of the bimorph layers. However, most of the commercially available monocrystalline LN and LT wafers are cuts obtained by rotating the crystal at a certain angle about the $x$ axis, and the $y'$ axis is taken as the normal to the plate (the number of dashes in the name of the axis means the number of rotations of the coordinate system, as a result of which this axis or material constant is obtained). In this regard, below, the $y'$ axis is taken as the direction of the application of the electric field, and the $z$ axis (piezomodule $d_{33}$) is taken as the direction of the deformation. Hence it follows that the sought values of the dielectric constant tensor and the elastic compliance matrix will be $\varepsilon_{22}^T$ and $s_{13}^E$, respectively.

Following the reasoning presented in [23, 201, 204], we consider a ferroelectric crystal belonging to the space symmetry group 3R3c. The crystal is made in the form of a rectangular plate with linear dimensions $l \times w \times t$ (length, width, and thickness, respectively). Let us direct the $x''$, $y''$, and $z''$ axes of the Cartesian coordinate system along the edges of the plate as shown in Fig. 20.

The value of the tensor quantity unknown in the $x''$, $y''$, $z''$ coordinate system is determined by the sequence and angles of rotation of the original $x$, $y$, $z$ coordinate system, for which the values of the required tensor quantity are known. The formulas for calculating the value of a tensor in a rotated coordinate system depend on the rank of the tensor:

— the dielectric tensor $\varepsilon_{ij}$ (rank 2):

$$\varepsilon_{kl} = a_{\alpha\beta} \varepsilon_{ij}^{\alpha\beta},$$

(19)

— the tensor of piezoelectric coefficients $d_{ijk}$ (rank 3):

$$d_{lmn} = a_{\alpha\beta\gamma} d_{ij\alpha} a_{\beta\gamma\delta} d_{kg\delta},$$

(20)

— the elastic compliance tensor $s_{ijkl}$ (rank 4):

$$s_{mnop} = a_{m\alpha} a_{n\beta} a_{o\gamma} a_{p\delta} s_{ijkl}^{\alpha\beta\gamma\delta},$$

(21)

where $a_{\alpha\beta}$ ($\alpha, \beta \in \{1,2,3\}$) are the values of the direction cosine matrices of rotation. Formulas (19)–(21) imply summation over repeated indices (Einstein’s rule).

To calculate the values of the material constants in the cuts rotated around the $x'$ axis and having the $y'$ axis as the normal to the plane, we need to successively carry out two rotations, which together are determined by the matrix

$$a = a_x a_y,$$

(22)

where

$$a_x = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\alpha & -\sin\alpha \\ 0 & \sin\alpha & \cos\alpha \end{pmatrix}, \quad a_y = \begin{pmatrix} \cos\varphi & 0 & -\sin\varphi \\ 0 & 1 & 0 \\ \sin\varphi & 0 & \cos\varphi \end{pmatrix}$$
are the matrices of the rotation of the coordinate system around the \( x \) and \( y' \) axes, respectively.

Then the matrix of rotation \( a \) will have the form
\[
a = \begin{pmatrix}
\cos \varphi & \sin \varphi \sin \alpha & -\sin \varphi \cos \alpha \\
0 & \cos \alpha & \sin \alpha \\
\sin \varphi & -\cos \varphi \sin \alpha & \cos \varphi \cos \alpha
\end{pmatrix}.
\]

(23)

Taking into account the nature of the recording of the required quantities \( \varepsilon_{22}^T \), \( d_{23} \), and \( s_{33}^E \) for crystals belonging to the point group \( 3m \), in the standard setting, as well as the transformation rules from the matrix notations to tensor notations and vice versa [187], we obtain the following angular dependences:

— the dielectric tensor:
\[
\varepsilon_{22}^T (\alpha) = \varepsilon_{11}^T \cos^2 \alpha + \varepsilon_{33}^T \sin^2 \alpha,
\]

(24)

—the matrix of piezoelectric coefficients:
\[
d_{23} (\alpha, \varphi) = \sin^2 \varphi (-d_{23} \cos \alpha + d_{31} \sin \alpha) + \cos^2 \varphi
\times (-d_{15} \sin \alpha \cos^2 \alpha + d_{22} \sin^2 \alpha \cos \alpha
\]
\[
+ d_{31} \sin^3 \alpha + d_{33} \sin \alpha \cos^2 \alpha),
\]

(25)

—the matrix of elastic compliance:
\[
s_{33}^E (\alpha, \varphi) = s_{31}^E (a_{11}^2 + a_{22}^2 + a_{33}^2 + 2a_{13}^2 + s_{44}^E)
\times a_{33}^2 + a_{12}^2 + 2a_{14}^2 \left[ a_{13}^2 - a_{12}^2 \right].
\]

(26)

The values of the material constants of the LN and LT crystals in the standard setting are given in Table 1.

Using formulas (24)–(26), we can calculate the values \( \varepsilon_{22}^T, d_{23}, \) and \( s_{33}^E \), as well as the value of the ratio \( d_{23}/(s_{33}^E \varepsilon_{22}^T) \) for all commercially available LN and LT cuts. Let us look at some of these angular dependences.

Figure 21 shows the graphs of the change in the coefficient of the dielectric constant \( \varepsilon_{22}^T \), corresponding to the direction of application of the electric field normal to the plane of the plate. Obviously, the minimum values \( \varepsilon_{22}^T \) are achieved when the crystal is rotated around the axis \( x \) at 90° and 270° (z-cut). In this case, for LT crystals, the change in the dielectric constant upon rotation through angle \( \alpha \) is rather small and can be neglected in a number of cases. Among commercial \( y + \alpha \)-cuts, the smallest value \( \varepsilon_{22}^T \) of LN is achieved in the \( y + 64° \) and \( y + 127.86° \)-cuts.

The angular dependences \( s_{33}^E (\alpha, \varphi = 0) \) exhibit a more complex behavior (Fig. 22). A peculiarity is the presence of the maximum in the area of the commercial cut with \( \alpha = 127.86° \) on the graph plotted for LN. Among the commercially available cuts, the minimum values \( s_{33}^E \) are observed in cuts \( y + 64° \) and \( y + 163° \) for LN and at cut \( y + 36° \) for LT. It should be noted that, just as in the case of the dielectric permeability \( \varepsilon_{22}^T \), the change in elastic compliance \( s_{33}^E \) when rotating around the axis \( x \) is small in LT crystals. In addition, the smaller value \( s_{33}^E \), in comparison with LN, allows us to partially compensate the lower values of the piezoelectric coefficient \( d_{23} \) of the LT crystal (see below).

Among the characteristics responsible for the suitability of the BC for use in sensors and actuators, the determining factor is the transverse piezoelectric coefficient. Indeed, unlike \( \varepsilon_{22}^T \) and \( s_{33}^E \), which, depending on the cut of the crystal, change by tens of percent, the value \( d_{23} \) in LN crosses zero three times when the coordinate system is rotated around the \( x \) axis by an angle of \( 0° \leq \alpha \leq 180° \), increasing to a value of \( \approx 30 \) pC/N in the case of the \( y + 140° \)-cut. For an LT crystal, the range of variation of the transverse piezomodule is not as large; however, in this case also, \( d_{23} \) varies from 0 to \( \approx 10 \) pC/N (Fig. 23).

Coefficients \( \varepsilon_{22}^T \) and \( d_{23} \) in any fixed cut \( y + \alpha \) also change upon rotation through angle \( \varphi \) around the normal to the plane of the crystal plate. This leads to the fact that, for the creation of the device, not only the correct choice of the cut becomes important but also the orientation of the long side of the BC relative to the \( x \) axis (fixed at the first rotation through angle \( \alpha \)). In particular, the change in the sign of the piezoelectric coefficient \( d_{23} \) when rotating around axis \( y' \) by angle \( \varphi = 56.2° \) leads to a saddle-like deformation of the bidomain plates [204] and the possibility of manufacturing torsion actuators based on them [206].

Table 2 shows the values of the material constants for various commercial LN and LT cuts.
The pseudo-three-dimensional dependence of the ratio \( \frac{d_{23}}{(s_{33}^{E}s_{22}^{T})} \) and CEMS \( k_{23} \) on the angles of rotation \( \alpha \) and \( \varphi \), plotted for crystals LN and LT, are presented in Fig. 24. Analysis of these dependences allows us to establish that, in terms of manufacturing sensors and actuators in which the BCs are used as a bending bimorph, the cuts \( y + 130.5^\circ \) in LN and \( y + 135.2^\circ \) in LT are the best. In this case, due to the lower values of the dielectric constant \( \varepsilon_{22}^{T} \) and elastic compliance \( s_{33}^{E} \) in LT, ratio \( \frac{d_{23}}{(s_{33}^{E}s_{22}^{T})} \) in it is only 50% lower than in LN. Together with their higher temperature stability, this makes LT crystals promising for manufacturing devices based on BCs. To create devices operating at the bending resonance frequency, the best (maximum CEMS) cuts are the \( y + 136.6^\circ \)-cut of LN and the \( y + 136.4^\circ \)-cut of LT.

Obviously, among the commercially available \( y + 127.86^\circ \)-cut of LN is the best cut for making BCs used as bending bimorphs. At the same time, crystallographic sections of LT, close to the optimal \( y + 135.4^\circ \)-cut, is not widely sold. The best commercially available cut in this case is the \( y + 36^\circ \)-cut, for which, however, the
value \( |d_{23}|/(s_{33}E_{22}) \) is much lower and amounts to 0.0295 \((\varphi = 123^\circ)\), and the CEMS value is \(k_{23} \approx 0.1489 \) \((\varphi = 90^\circ)\). Note that in the \(y + 36^\circ\)- and \(y + 42^\circ\)-cuts of LT, the maximum values of the piezoelectric coefficient \(d_{23}\) are achieved when \(\varphi = 90^\circ\) and are \(-6.84\) and \(-6.54\) pC/N, respectively.

APPLICATION OF BIDOMAIN CRYSTALS

LN and LT BCs are promising for a whole range of applications as efficient mechanoelectrical converters with stable properties and reproducible characteristics. This is achieved due to the monocrystalline nature and unique spectrum of the properties of LN and LT, as well as the well-developed technology for producing massive single crystals for optics and acoustics. Due to the lower values of the piezoelectric coefficients and the higher complexity of the formation of the bidomain structure, LT crystals are practically not considered in the literature as bimorph transducers. However, higher chemical and temperature stability and lower electrical conductivity make LT a promising material for devices operating in high temperatures and aggressive environments. In what follows, a BC is understood to mean a lithium niobate crystal, unless otherwise stated.

The most obvious application of BCs is the creation of precision actuators based on them. A linear dependence of the deformation on the applied potential difference is observed, in principle, for glued or sintered composite actuators [207, 208]. However, the maximum possible thermal stability, mechanical strength, and quality during deformation at the resonant frequency can be achieved only in the absence of any phase boundaries. The idea of using a single-crys-

Table 2. The calculated values of \(d_{23}\), \(e_{22}^T\), and \(s_{33}^E\) for various commercially available LN and LT cuts

| Material | Cut       | \(d_{23}\), pC/N | \(s_{33}^E\), TPa\(^{-1}\) | \(e_{22}^T\) | \(|d_{23}|/(s_{33}e_{22}^T)|\), C/m\(^2\) | \(k_{23} = \sqrt{|d_{23}|/(s_{33}e_{22}^T)|}\) |
|----------|-----------|-----------------|-----------------|-------------|---------------------------------|-----------------|
| LN       | \(z (= y + 90^\circ)\) | -2.00           | 4.36            | 51.00       | 0.0091                           | 0.0454          |
|          | \(y + 36^\circ\)       | -5.57           | 4.54            | 48.92       | 0.0242                           | 0.1213          |
|          | \(y + 42^\circ\)       | -4.92           | 4.64            | 48.31       | 0.0219                           | 0.1105          |
|          | \(y + 64^\circ\)       | -3.00           | 5.49            | 40.38       | 0.0180                           | 0.0903          |
|          | \(y + 127.86^\circ\)   | -26.96          | 6.88            | 50.34       | 0.0779                           | 0.4872          |
|          | \(y + 163^\circ\)      | -18.32          | 5.39            | 79.38       | 0.0428                           | 0.2977          |
| LT       | \(z (= y + 90^\circ)\) | -2.00           | 4.36            | 51.00       | 0.0091                           | 0.0454          |
|          | \(y + 36^\circ\)       | -5.37           | 4.54            | 48.92       | 0.0242                           | 0.1213          |
|          | \(y + 42^\circ\)       | -4.92           | 4.64            | 48.31       | 0.0219                           | 0.1105          |

The calculation was carried out using formulas (24)–(26) for room temperature and \(\varphi = 0\).
Fig. 24. Dependences of relationship $|d_{23}/(s_{33}E_{22})|$ (a, b) and CEMS (c, d) at room temperature on the rotation angles $\alpha$ and $\varphi$, calculated for LN (a, c) crystals and in LT (b, d).
tal bimorph to perform precise displacements was proposed almost immediately after the discovery of the possibility of forming a bidomain structure in large-area plates using diffusion annealing [203].

The simplest single-crystal bimorph actuator is a BC of the optimal crystallographic cut with solid electrodes applied to the polar faces. The largest piezoelectric modulus $d_{23}$ is achieved in the crystal LN $y + 140^\circ$-cut, i.e., the greatest displacement under bending deformation, according to Eq. (14), can be obtained on a rectangular cantilever-mounted BC of this cut with the long side perpendicular to the $x$ axis. In [209], such an actuator was fabricated based on a bidomain plate of the LN $y + 140^\circ$-cut (annealing in humid argon for 10 h at 1140°C). The movement of the free end of the bending cantilever 7.3 mm long and 0.5 mm thick was about $7.5 \mu$m at a voltage of 100 V and practically did not differ from the value obtained from Eq. (14). The value of the creep was very small, and the maximum amplitude of deformation when an electric voltage was applied was reached almost instantly. Later, linearity, as well as the absence of hysteresis and creep, was repeatedly confirmed in the works of other authors, including works on crystals of the commercially available $y + 128^\circ$-cut and on crystals of the $y + 165^\circ$-cut (Fig. 25) [77, 210].

Due to the absence of creep, a step change in the voltage across the console actuator leads to the appearance of high-Q oscillations at the resonant frequency. The simplest way to damp such vibrations is mechanical damping [210].

The rectangular BC $y + 128^\circ$-cut (or another with a similar angle of rotation), cut in a way that the long side is rotated around the normal to the plate at an angle $\varphi \approx 55^\circ$ allows the implementation of an actuator capable of rotating around the bimorph axis (Fig. 26). The angle of rotation $\psi$ linearly depends on the applied voltage and can be determined by the formula

$$\psi = \frac{3}{2} d_{23} V_{\text{ext}} \frac{l}{l_0}. \tag{27}$$

The experimental dependence $\psi(V_{\text{ext}})$ almost coincides with that calculated by Eq. (27), and the angle of rotation can reach several degrees without any saturation [206, 211, 212].

Examples of the successful use of actuators based on BCs include a system for the mechanical switching of optical fibers (response time 10 ms) [210], a beam deflection system for an X-ray diffractometer [213–216], a three-coordinate positioning device for a probe microscope [217, 218], an actuator for stretching biological objects [219], and a rotary optical filter based on the Fabricare–Pero standard [211].

In the oscillatory mode, BC-based consoles demonstrate a high Q-factor and transverse CEMS ($k_{31} = 0.51$ in crystals of the LN $y + 137^\circ$-cut), which is higher than the values for common brands of piezoelectric ceramics PZT-5H, PZT-4, and PZT-8 [220].

Due to this, piezoelectric oscillators with a lower capacitance coefficient (the ratio of static capacitance to dynamic capacitance at the first resonant frequency for the $y + 128^\circ$-cut is $C_0/C_k = 7.02$ and can be further reduced by changing the configuration of the electrodes), which may be of interest in order to create piezoelectric generators [203].

As noted earlier, the presence of a bidomain structure in a crystal leads to the excitation of even harmonics of thickness vibrations with the complete disappearance of odd harmonics in the case of an interdomain boundary in the middle of the plate. In this case,
even overtones, for which half the wavelength is close to half the thickness of the plate, are excited with a much larger vibration amplitude than odd overtones in a single-domain plate. Therefore, sufficiently thin BCs can be used as effective high-frequency resonators and ultrasonic transducers [33]. An important advantage of ultrasonic devices based on BCs operating in the mode of thickness vibrations is a significant decrease in the intensity of the so-called false modes of vibrations that arise in single-domain plates due to the interference of various types of vibrations [221]. In addition, a thin inverse domain acts as a waveguide for a surface acoustic wave, which makes it possible to concentrate the wave energy at the surface and reduce the temperature coefficient of the delay [22]. The theoretical analysis of oscillatory processes is presented in detail in [222–225].

An original design with the local inversion in the LN crystal of the $y + 36^\circ$-cut has been successfully used for the simultaneous emission and reception of acoustic radiation in an ultrasonic harmonic imaging device [192]. The possibility of forming a near-surface domain by annealing with a titanium mask made it possible to realize the active part of the device in one single-crystal plate (Fig. 27). The noninverted area surrounded the inverse region and served as an ultrasound emitter at the fundamental frequency. The section of the crystal with the formed inverse domain was the second harmonic receiver of the reflected radiation. The efficiency of the reception of the second harmonic was due to the property of the BC region to be excited on the even overtones of the thickness vibrations. The authors have obtained a significant improvement in the quality of the ultrasound image in comparison with a similar transducer based on a single-domain crystal.

In [226], a construction of a piezoelectric gyroscope based on a bidomain plate of the $z$-cut was proposed. Due to the equality of the piezoelectric shear coefficients and the symmetry of the mechanical properties in the plane of the plate, shear vibrations of the same frequency are excited in perpendicular directions. Due to the absence of odd overtones, the Coriolis force related to the rotation is balanced inside the crystal and is not transmitted to the fixing system, which improves the stability of the gyroscope and increases the oscillation Q-factor.

A number of studies also noted the possibility of generating the second harmonic of laser radiation with a conversion efficiency of up to 18% W on near-surface RDSs consisting of inverse domains obtained by diffusion annealing [98, 101, 151]. In addition, a number of solutions have been proposed for the creation of high-frequency resonators and reflectors based on near-surface RDSs for use in devices based on bulk and surface acoustic waves [22, 23, 33]. However, these applications have not been developed further in connection with the emergence of methods for the formation of RDSs of a higher quality without the need to heat crystals to high temperatures.

BCs can be used not only as precision actuators but also in the direct piezoelectric effect mode in sensors and waste energy collection systems. The potential difference across the electrodes of a monocrystalline bimorph linearly depends on the magnitude of its bending and can be used as a useful signal. In the static mode (the deformation of the BC does not change in time), the voltage generated as a result of the piezoelectric response will decrease over time due to the leakage of charges over the volume, surface, and (if present) the measuring circuit. Despite the rather high resistance of LN and LT at room temperature, the ability to place the sensitive element of the sensor in a vacuum or dry inert gas and the availability of voltage meters with a high-resistance input on the field-effect transistors on the market, it is impossible to completely eliminate the drain of charges. This limits the use of BCs as statically deformable sensors.

In contrast, the periodically changing bend of the BC can be measured in the form of an electric signal at frequencies of several Hz, which finds application in sensors of ultraweak vibrations and sensors of weak magnetic fields with the sensitive element based on the BC. In addition, the efficiency of the transformation of the deformation into stress makes it possible to create devices for collecting waste energy based on BCs for powering low-power autonomous devices.
The simplest design of a highly sensitive vibration sensor with a bidomain LN crystal as a sensing element is a monocrystalline bimorph fixed on a base in the form of a beam, which is deformed due to the vibration of the fastening system. In order to increase the rigidity and thermal stability, the fastening system can be made of sapphire or corundum ceramics of the VK-100 type. The functioning of such a sensor was investigated theoretically and experimentally in [19, 201, 227].

Two methods have been proposed for transmitting the vibration effect to the sensitive element. In the first case, the crystal is fixed on both sides, and one of the fastenings is motionless during the vibration, and the second one performs reciprocating movements together with the vibrating object (Fig. 28a) [227]. In the second scheme, the crystal is cantilevered in a rigid holder and is excited by the vibration of the device as a whole (Fig. 28b) [19].

The prototype sensor, in which the movement of the quasi-free end of the bimorph was carried out using a rod, demonstrated a rather low sensitivity (~0.28 V/g at the resonant frequency, \( g = 9.8 \text{ m/s}^2 \) is the acceleration of gravity). However, despite the complexity of the design, the operating frequency range of such a sensor is somewhat wider than that of a simple console (in [227], the resonant frequency for a crystal 70 mm long and 0.5 mm thick was reached at 500 Hz).

The disadvantage of the simple cantilever design is the low resonant frequency and lower rigidity compared to a double-sided mounting. At the same time, it is in this configuration that the maximum sensitivity is achieved and it becomes possible to measure ultrasonic oscillations far from resonance. The sensor studied in [19] with the sensitive element made of a bidomain crystal of an LN \( y + 128^\circ \)-cut with a working part length of 70 mm and a thickness of 0.5 mm when measured with a lock-in amplifier demonstrated the ability to reliably detect sinusoidal vibrations with an amplitude of 0.1 nm at frequencies above 38 Hz, and with an amplitude of 100 nm at frequencies above 7 Hz. At the resonant frequency (~97 Hz), the sensor’s sensitivity was 2443 V/g, far from resonance of 7 V/g, which is a record value for this type of sensor. It is obvious that the use of a high-impedance preamplifier stage and the use of differential circuits can increase the sensitivity by about an order of magnitude.

One of the important advantages of vibration sensors using the piezoelectric effect is their low cost compared to interferometric noncontact vibrometers. However, the presence of adhesive bonds in composite bimorphs reduces the sensitivity and reproducibility of the results, especially under conditions of varying temperatures and significant vibration amplitudes. An advantage of sensors with a sensing element based on a BC is the closeness of the transfer characteristic to the ideal case described by fairly simple models [201].

Another promising direction of using bidomain ferroelectric single crystals in sensorics is the creation of magnetoelastic composites based on them for highly sensitive sensors of ultralow magnetic fields. The magnetoelastic effect in such composites arises due to the elastic bond between the magnetostrictive material and the piezoelectric. To obtain a magnetoelastic composite based on a bidomain LN crystal, it is glued with an epoxy composition with a foil of a ferromagnet with a significant magnetostriction value and a small saturation magnetostriction field (for example, amorphous strips of the Metglas alloy with the Fe_{70.2}Co_{7.8}Si_{12}B_{10} composition). Such a composite, when placed in a magnetic field, is deformed under the action of the magnetostrictive effect, which leads to the appearance of a potential difference on the polar

![Fig. 28. Vibration sensor designs with a bidomain LN crystal as a sensing element, investigated in [227] (a) and [19] (b).](image-url)
faces of the piezoelectric crystal. An important advantage of using a BC over a single-domain crystal is the addition of the electric fields of two domains when the plate is bent by a deforming magnetostrictor (Fig. 29). The main qualitative characteristic of a magnetoelastic composite based on a BC is the coefficient $\alpha_{E32}$ of the matrix of magnetoelectric coefficients (here we use the coordinate system accepted in the literature, in which the $x_2$ axis corresponds to the direction of the deformation of tension-compression under the action of magnetostriction, and the $x_3$ axis perpendicular to the faces from which the potential difference is removed; to convert this notation to the one introduced above for cuts of plates rotated around the $x_1$ axis, it is sufficient to swap indices 2 and 3).

The ability of a magnetoelectric composite material to convert magnetic field energy into an electrical signal can be used in highly sensitive magnetic sensors that do not require cooling. In the simplest case, such a sensor has a design similar to a vibration sensor, except that the useful signal that deforms the crystal is the magnetic field strength, and vibration is a spurious signal and should be minimized. As in the case of vibration sensors, the presence of charge leakage makes it difficult to measure constant magnetic fields (although there are techniques to circumvent this limitation [228]), and the sensitivity to low-frequency alternating fields, in contrast, is high due to the presence of low-frequency flexural resonance modes.

The first study of two-layer magnetoelectric composites based on a BC was presented in [229]. The authors compared the magnetoelectric response from the piezoelectric–Metglas samples, where the role of the piezoelectric was played by BCs with the head-to-head and tail-to-tail structures, as well as single-domain crystals and glued bimorphs. The samples based on BCs had a magnetoelectric coefficient of $\alpha_{E32} = 578$ V/(cm Oe) at the frequency of mechanical resonance, which is twice as high as in the samples studied in this study on bimorph and single-domain crystals. Later, the idea of using magnetoelectric composites for detecting superweak magnetic fields was implemented in [230, 231] on rectangular sensitive elements in a cantilever and point mounting.

As noted above, although the rotated LN $\gamma + 128^\circ$-cut is optimal among the commercially available cuts for the creation of mechanoelectrical converters, the highest value of the CEMS ratio is achieved in the $\gamma + 136.6^\circ$-cut and the highest value of the piezomodule $d_{33}$ is achieved in the $\gamma + 140^\circ$-cut close to it. In [232], a magnetoelectric composite based on the BC $\gamma + 140^\circ$-cut was studied. The maximum value of the magnetoelectric coefficient for a structure with a piezoelectric phase size of $20 \times 5 \times 0.42$ mm$^3$ at the antiresonance frequency was 1704 V/(cm Oe), and the manufactured prototype of the magnetic sensor demonstrated the possibility of measuring a record low magnetic field for such structures of $\sim 200$ fT.

The main problem when measuring ultraweak magnetic fields is external noise. At the same time, when using a magnetoelectric composite with a piezoelectric BC, a significant contribution of acoustic spurious signals related to the detection of vibrations of the holder and the environment is added to the external electromagnetic interference and internal noise of the measuring system. One of the interesting solutions to reduce the level of acoustic noise in magnetic field sensors based on magnetoelectric composites is the use of a tuning fork design, which makes it possible to obtain a “differential” measurement at the mechanical level. The homogeneity of the properties of single-crystal LN and modern techniques for the formation of a bidomain structure make it possible to create self-consistent tuning fork structures by a simple longitudinal cutting of the bimorph [233]. The contribution of acoustic noise is reduced due to the fact that the tuning fork’s teeth are separate sensors with very sim-
ilar characteristics and the same fixing conditions, but with the antiparallel application of magnetostrictive layers. The external vibrations cause the teeth to oscillate in phase, while the useful signal causes antiphase movement of the teeth (Fig. 30). With the correct electrical connection of the tuning fork’s teeth, this design permits the sensitivity of the sensor to increase by an order of magnitude without the use of any external processing electronics [234].

Special attention should be paid to the possibility of using bidomain crystals and composite structures based on them to collect waste energy. Reducing the energy consumption of modern microelectronic devices makes it promising to create autonomous systems that can be powered by the energy received from external noise sources (mainly of man-made origin) without involving chemical batteries or connecting to the power grid. Similar designs to the vibration and magnetic field sensors described above can efficiently convert ambient acoustic or electromagnetic noise into electrical energy and can be used to power low-power devices. Since most of the target noise sources (motors, shafts, seismic vibrations of technogenic origin) have significant amplitudes in the low-frequency region of the spectrum, cantilever-mounted transducers are used in waste energy collection devices.

The ability to efficiently convert vibrations into electricity using a BC was demonstrated in [235, 236]. Comparison with single-domain samples and glued bimorphs based on PZT ceramics that have a similar geometry showed a significant advantage of the BC. The piezoelectric material was attached to a spring steel plate and the maximum average power was examined for various levels of vibration excitation and matched load ratings. The maximum average power of converters based on a lithium niobate BC was 9.2 mW/g²; for single-domain LN samples, 6.2 mW/g²; and for PZT ceramics, 1.8 mW/g² [235]. Tests on the collection of vibration energy from an industrial compressor under conditions of a wide vibration spectrum and unmatched load have shown the possibility of generating power in units of nW at a BC 32 mm long and 0.5 mm thick [236]. To increase the efficiency of energy collection from sources of electromagnetic radiation, the structure can be supplemented with a magnetostrictive layer [237].

Due to the efficiency of the conversion of mechanical deformation into an electrical signal and resistance to cyclic deformations, a BC can be used to collect the energy of radioactive β-decay. In the design proposed in the patent [238], a thin foil of a radioactive substance undergoing β-decay (for example, an $^{63}$Ni isotope), was placed under the cantilever made of BC. The electrons emitted by the isotope charge the gap between the foil and the bidomain crystal, and the latter bends under the action of an electrostatic force. By correctly choosing the size of the gap (several tens of microns) and the length of the bidomain cantilever, it is possible to force the free end of the crystal to periodically touch the surface of the radioactive foil, causing a short circuit with the accompanying discharge of the gap, and, as a consequence, straightening and oscillations of the cantilever under the action of elastic forces. The generated electrical signal can have a sufficiently large amplitude, which is an important advantage over semiconductor β-voltaic sources, the output voltage of which is limited by the height of the potential barrier by the $p–n$-transition or the Schottky barrier.

One of the important tasks facing the developers of sensors and actuators based on a BC is the organization of the crystal fixation in such a way as not to...
negate the lack of hysteresis, linearity, or temperature stability. In particular, gluing the crystal to the holder leads to a significant creep [210]. Therefore, in order to obtain the best characteristics of devices based on a BC, it is necessary to connect the crystals to the base either by soldering or using rigid clamps. The latter option is often difficult, especially when working with thin crystals. One of the possible solutions in this case may be a local thinning of the working part of the crystal to the required thickness while maintaining the original thickness in the area intended for fixing. In this case, the holder will be the thicker part of the crystal, and the properties of such a holder will approach the ideal properties.

CONCLUSIONS

Thus, the use of LN and LT crystals is not limited to optics or high-frequency acoustics. The stability of the properties and manufacturability of these materials, as well as their unique ferroelectric properties, can be used to create sensors and actuators based on crystals with a bidomain structure. Such a structure can be formed by a number of different techniques, the main common feature of which is the creation of a certain force field in the crystal, which is determined by the gradient of the property (for example, the concentration of the point defects or impurity atoms) or action of the temperature or electric field. A bidomain structure can be formed in the entire crystal or in the specified near-surface regions using a mask. Depending on the area of further application, a bidomain structure can be formed in various crystallographic sections. The main requirement for a cut, which must be fulfilled to create a BC, is the presence of a nonzero projection of the optical axis onto the normal to the plane of the plate. Depending on the chosen orientation of the crystal based on the BC, highly sensitive vibration and magnetic field sensors, precision bending and rotational actuators, waste energy collection devices, acoustic transducers, filters, and resonators can be manufactured.

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