
<https://doi.org/10.15407/ujpe71.10.779>

S.O. VORONOV, YU.M. POPLAVKO

National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute"
(37, Beresteivskyi Ave., Kyiv 03056, Ukraine)

CONFIGURATIONAL ENTROPY APPLICATION TO EXPLAIN POLAR CRYSTALS PECULIARITIES

Polar crystals possess a unique ability to acquire electrical polarization by means of non-electrical influences: mechanical, thermal, optical, and other impacts. Polar crystals are also capable of mutual transformation of mechanical, thermal and electrical energy, demonstrating piezoelectric and pyroelectric effects (both direct and inverse). The electrical parameters of polar crystals strongly depend on the mechanical and thermal conditions of the experiment and, conversely, their thermal and elastic properties are determined by electrical conditions. In this paper, the unique properties of polar crystals are analyzed using experimental data and thermodynamics. In particular, the intrinsic polarity of crystals is explained by the difference in electronegativity of neighboring ions in the crystal lattice, and by self-organization of dynamic polar clusters that is explained by the concept of configurational entropy. These considerations were illustrated by some examples: the influence of external conditions on the properties of polar crystals, the increase in volume of the polar state, and the high permittivity of relaxor ferroelectrics.

Keywords: polar crystals, piezoelectrics, pyroelectrics, ferroelectrics, electronegativity, configurational entropy, relaxor ferroelectrics.

1. Introduction

Electrically polar materials (crystals, polarized ceramics, thin films, liquid crystals, etc.) are widely used in electronics, stimulating research into them [1]. Fundamental physical research should naturally be conducted on polar crystals, and it should be noted that the manifestations of their polar properties are complex and diverse phenomena. The polar crystals manifest themselves in many fundamental properties, not just electrical ones. These properties include pri-

marily mechanical and thermal phenomena, where the polarity of the crystals leads to piezoelectric and pyroelectric effects [2]. They are conditioned by peculiar interionic polar bonds which are strictly directed, which reduces the coordination number of the crystal lattice, and also leads to its less dense structure with a high anharmonicity of lattice vibrations.

The goal of this work is to come closer to explaining the causes and patterns that contribute to the emergence of polar structures in certain crystals, as well as to explain their unusual properties using experiments and thermodynamics. Theoretical concepts include the electronegativity of atoms, which ensures the polar bond between a cation and an anion in the crystal lattice, and the configurational entropy that accompanies the formation of dynamic polar clusters in crystals (which arise and are destroyed by thermal vibrations of the crystal lattice).

Citation: Voronov S.O., Poplavko Yu.M. Configurational entropy application to explain polar crystals peculiarities. *Ukr. J. Phys.* **71**, No. 10, 779 (2026). <https://doi.org/10.15407/ujpe71.10.779>.

© Publisher PH "Akadempriodyka" of the NAS of Ukraine, 2026. This is an open access article under the CC BY-NC-ND license (<https://creativecommons.org/licenses/by-nc-nd/4.0/>)

1.1. Electronegativity

The tendency of an atom to attract shared electrons in a chemical bond is customarily called electronegativity. It characterizes the atom's ability to attract electrons toward itself, which greatly influences the strength of the formed interatomic or interionic bond. Electronegativity is influenced by the charge of the nucleus and the arrangement of electrons in the inner electron shells, which determine the distance of valence electrons from the nucleus and thereby determine the degree of shielding of valence electrons from the positively charged nucleus.

In usual molecular and metallic crystals, consisting of particles with the same electronegativity, a highly symmetrical (usually cubic) structure with a maximal coordination number of 12 is formed. But crystals consisting of ions with significantly different electronegativities are predisposed to the formation of polar bonds; accordingly, they have more complex structures with lower coordination numbers (usually 6–8). In polar crystals with mixed covalent-ionic bonds, the charge separation between neighboring ions is determined by the fact that the cation is significantly more positive and the anion is more negative than would follow from their formal valence, and the coordination number can decrease to 4–6.

Electronegativity is a chemical property that influences the type of bond that forms between atoms; a small difference in the electronegativity of neighboring atoms promotes covalent bond formation, an increased difference leads to an ionic bond, while a very large difference in the electronegativity of neighboring ions promotes polar bond formation. Thus, the difference in electronegativity contributes to a specific distribution of interatomic electron density. Polar-sensitive structures manifest themselves in crystals as the ability to give an electric (vectorial) response to the nonelectric scalar effects (or to more complex tensor-type effects). Hybridized ionic-covalent bonding causes a decrease in the symmetry of the crystal, so polar crystals always belong to noncentrosymmetric classes. Moreover, it is the presence of such bonds that determines the noncentrosymmetric structure of crystals. Therefore, hybridized ionic-covalent bonding is the main cause of pyroelectric and piezoelectric properties. This is based on the asymmetry in the distribution of electronic density along the atomic bonds, which ensures the ability of the crystal

to give a polar (electric) response to nonelectric effects.

It can also be concluded that the internal polarity, observed in polar crystals, arises as a structural compensation for the different electronegativity of neighboring ions [3].

1.2. Configurational entropy

Among the thermal, mechanical and electrical behaviors of polar materials, some properties appear so unique that they could be explained only by assuming that thermal motion in polar crystals leads to a complex self-organization of interatomic bonds into dynamic groups or clusters.

The specific *electrical* properties of polar crystals (except for piezoelectric and pyroelectric effects) include, firstly, the anomalously high microwave absorption of the quasi-Debye type; secondly, the anisotropy of permittivity in most polar crystals; thirdly, the gigantic value of the permittivity at the Curie point in ferroelectrics with a second-order phase transition, as well as in relaxor ferroelectrics.

The specific *mechanical* properties of polar crystals include, firstly, a several-fold decrease in the elastic wave velocity that indicates a decrease in the elastic constant with a pronounced minimum in the region of the phase transition to the nonpolar phase. Secondly, hydrostatic pressure lowers the temperature of the ferroelectric phase transition, as if “squeezing out” the ordered polar phase, facilitating its transformation into a disordered phase. In contrast, the temperature of the antiferroelectric phase transition increases under the influence of hydrostatic pressure, which thus promotes antipolarity.

The specific *thermal* properties of polar crystals include firstly, a maximum of heat capacity observed near the phase transition from the nonpolar state to the polar phase (exactly as in the case of magnetic ordering in ferromagnets). Secondly, the thermal diffusivity in polar materials is tens of times lower than in nonpolar crystals, and decreases critically near the phase transition. Thirdly, the negative coefficient of volume thermal expansion is observed (usually in the temperature range around $0.1\theta_D$).

All the listed features support the application of the concept of configurational entropy. As is well known, the entropy of a thermodynamic system is defined as a measure of disorder in the system, de-

terminated by the number of states which individual particles can occupy. But it should be noted that the number of possible microstates in the system is also influenced by the self-ordering dynamics of the microgroups consisting of several combined particles. The latter leads to configurational entropy, which is a part of a system's total entropy related to the *arrangement* of its constituent particles rather than their motion. It is a measure of disorder arising from possible configurations, quantified by the number of possible arrangements. In this way, configurational entropy deals with positional disorder, while the vibrational (or "kinetic") entropy deals with disorder arising from particle motion.

Thus, in addition to the traditional "kinetic" entropy [4], associated with the motion of individual particles, there is an additional component of the total entropy, which is caused by the dynamic rearrangement of various nanoscale configurations. Moreover, the statistical probability of the existence of multiple self-coordinated states determines the entropy increase. This contribution to entropy corresponds to the multitude of ways of mutual arrangement of particles that support a certain general set of specified properties of the system. Thus, the configurational entropy, determined by the dynamic change in groups of constituent particles, is part of the total thermodynamic entropy of the system. In this case, the change in configurational entropy corresponds to the same change in total entropy.

The application of the above concepts to explain some of the special properties of polar crystals is discussed below.

2. Diverse Conditions Influence on Polar Crystal Properties

The conditions under which experiments with polar crystals are conducted (or under which they are applied) significantly affect all their parameters. Therefore, the boundary conditions under which these crystals are studied or applied must be strictly regulated [5].

These conditions can be mechanical, thermal or electrical.

2.1. Mechanical boundary conditions

One of these conditions assumes that the crystal is free to undergo any mechanical deformation (i.e., *stress-free*). This means that all components of the

2nd rank stress tensor X_{ij} are equal to zero: $X_{ij} = 0$. For a mechanically free crystal, this condition assumes the possibility of thermally or electrically induced deformation, so any component of the strain tensor x_{kl} is permitted. The parameters of a stress-free polar crystal are designated by superscript "X": permittivity ε^X , heat capacity C^X , thermal expansion coefficient α^X , elastic stiffness c^X etc. The equation of the converse piezoelectric effect is written as $x = d \cdot E$, where d is the piezoelectric modulus.

Another idealized mechanical condition is the crystal's impossibility of any deformation; in this case it is considered mechanically *clamped* and the crystal's strain tensor is $x_{kl} = 0$ (any deformation of the crystal is impossible). Obviously, in the static case (or at low frequencies) these conditions are practically impossible to ensure. But in real experiments, a polar crystal can be clamped by its own inertia, if its study is carried out at a frequency exceeding the natural electromechanical resonance frequencies of the crystal. The parameters of a mechanically clamped polar crystal are designated as ε^x , C^x , c^X etc. The equation of the converse piezoelectric effect is written as $X = e \times E$, where 2 is the piezoelectric constant.

The polarization induced by an electric field in a conventional dielectric is equal to $D = \varepsilon_0 \varepsilon E = \varepsilon_0 E + P$, but in the case of a piezoelectric it is necessary to take into account additional induction from the deformation of a mechanically free piezoelectric. For this purpose, one can use the equation of the direct piezoelectric effect: $P = -ex$, so the induction will be $D = \varepsilon_0 \varepsilon E + ex$. The electromechanical coupling to the stress X is characterized by the same piezoelectric constant e ; thus, in Hooke's law the inverse piezoelectric effect gives an additional stress: $X = cx - eE$. Since the crystal is free and its piezoelectric deformation has occurred, there is no mechanical stress in the piezoelectric ($X = 0$); therefore, from the last equation it follows that $x = eE/c$. Substituting this expression into the first equation, one can obtain:

$$D = \varepsilon_0 \varepsilon E + (e^2/c).$$

The above reasoning and an experimental example of the influence of mechanical conditions on permittivity are shown in Fig. 1.

From the above expression and Fig. 1, *a*, it follows that the mechanical response to the applied electric field enhances the dielectric induction. In a clamped

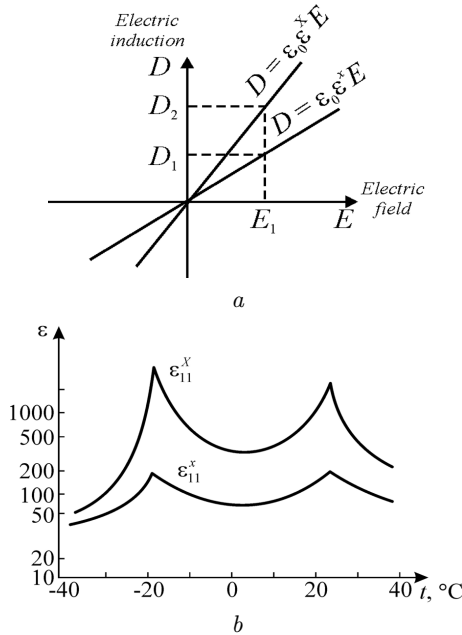


Fig. 1. Piezoelectric contribution to permittivity: electrical induction D dependence on electrical field E for free ($X = 0$) and clamped ($x = 0$) piezoelectric (a); temperature dependence of dielectric permittivity for free (at a frequency of 10^3 Hz) and clamped (at 10^{10} Hz) crystals of Rochelle Salt crystal $\text{KNa}(\text{C}_4\text{H}_4\text{O}_6) \cdot 4\text{H}_2\text{O}$ (b)

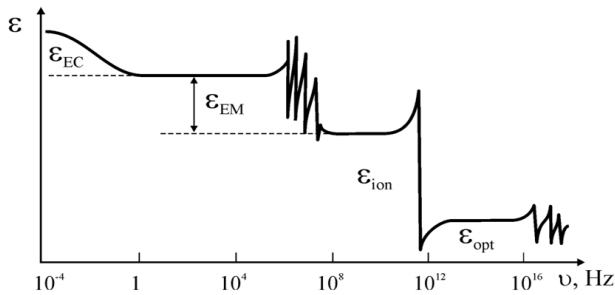


Fig. 2. Frequency dependence of the contributions to permittivity of some polarization mechanisms: ε_{opt} – electrons displacement; ε_{ion} – ions displacement; ε_{EM} – electromechanical polarization; ε_{EC} – electrocaloric polarization [7]

piezoelectric, in which deformation is impossible ($x = 0$), an external field E_1 induces $D_1 = \varepsilon_0 \varepsilon^x E_1$. In a free piezoelectric ($X = 0$), with the same field E_1 , the induction is greater: $D_2 = \varepsilon_0 \varepsilon^X E_1$.

The piezoelectric response appears as an additional polarization mechanism, since it mimics the corresponding contribution to the permittivity. If the piezoelectric is free, its permittivity is $\varepsilon = \varepsilon^X$, whereas in a mechanically clamped piezoelectric,

$\varepsilon = \varepsilon^x$. From the above equations, the following relationship between ε^x and ε^X is obtained:

$$\varepsilon^X = \varepsilon^x + e^2/\varepsilon_0.$$

Comparison of permittivity of free and clamped piezoelectrics is shown in Fig. 1, b. As an example, a well-studied ferroelectric is selected. The piezoelectric crystal Rochelle salt is studied over a broad temperature range; the permittivity of free and clamped crystals everywhere varies greatly. In the vicinity of the ferroelectric Curie points the clamping effect is particularly large: $\varepsilon^X/\varepsilon^x \approx 50$ [6]. At a lower frequency, ε^X is measured, because the piezoelectric reaction of the studied sample has enough time to be set freely ($X = 0$), and it contributes to the permittivity. At an ultra high frequency that is much higher than the frequencies of all piezoelectric resonances, the *mechanical inertia* of the test sample makes its piezoelectric deformation impossible in the external field ($x = 0$), and ε^x is determined.

The transition from increased permittivity ε^X obtained for a free crystal (at low frequencies) to the reduced permittivity ε^x inherent to a clamped crystal (at very high frequencies) is accompanied by many electromechanical resonances, Fig. 2. As an outstanding example, the KH_2PO_4 (KDP) crystal may be mentioned, because in this case the record ratio $\varepsilon^X/\varepsilon^x \approx 100$ is observed [6]. In a polar crystal free to undergo mechanical deformation, nothing prevents the dynamic reorientation of polar clusters in an electric field (characterized by configurational entropy), and therefore the permittivity is increased (ε^X). For the same reason, the inverse piezoelectric effect and the secondary pyroelectric effect in pyroelectrics manifest themselves freely in this case. Conversely, if deformation is impossible in a polar crystal, the contribution from configurational entropy is absent, the reorientation of polar clusters in an electric field is constrained, and the permittivity ε^x is determined experimentally. Likewise, the inverse piezoelectric effect manifests itself not in crystal deformation, but in the generation of mechanical stress, while in pyroelectrics, the secondary pyroelectric effect is impossible.

The difference between the permittivity of a free and a clamped crystal $\varepsilon^X - \varepsilon^x = \varepsilon_{\text{EM}}$ is called the electromechanical contribution to the permittivity. In the frequency characteristic $\varepsilon(f)$, this change appears as a sequence of multiple piezoelectric resonances, Fig. 2.

Thermal boundary conditions are important mainly for comparing theory (which usually uses thermodynamics) with experimental data, which are usually obtained from measurements in the kilohertz-to-megahertz frequency range. Accordingly, two limiting conditions of importance mainly for pyroelectrics can be analyzed.

The *isothermal* condition ($T = \text{const}$) assumes a constant temperature during the study or technical application of a polar crystal. For bulk samples, this condition is rarely met, since it is possible only at very low frequencies, when there is enough time for the energy exchange between the studied crystal and the environment. Nevertheless, in thermodynamic theories, it is convenient to consider polarization within the isothermal approximation. It should be noted, however, that isothermal conditions can be realized when studying and using very thin films in contact with a heat-conducting substrate, as well as when studying nanoscale objects.

The *adiabatic* approximation assumes constant entropy ($S = \text{const}$) when a pyroelectric or ferroelectric crystal is subjected to experimental conditions or used in an application. The entropy remains constant if there is no noticeable energy exchange between a polar crystal (or polar film) and the environment during one period of the varying influence when the object is being measured or operated. This is precisely the case when studying polar crystals at commonly used frequencies.

In a pyroelectric crystal, the apparent permittivity ε^T measured at low frequencies may contain a noticeable “electrothermal”, also called electrocaloric, contribution, Fig. 2. This refers to the difference $\varepsilon^T - \varepsilon^S = \varepsilon_{\text{EC}}$ between the permittivity ε^T measured under isothermal conditions, when $T = \text{const}$ and the dielectric has enough time to exchange energy with the environment, and ε^S measured under adiabatic conditions, at constant entropy $S = \text{const}$, i.e., when heat exchange is impossible [7].

Both ε_{EC} and ε_{EM} contribute to the “effective” permittivity ε_{ef} . This value does not correspond to the Lorentz’s definition of the parameter, which includes the permittivity resulting from the fundamental mechanisms of ionic ε_{ion} and electronic $\varepsilon_{\text{el}} = \varepsilon_{\text{opt}}$ polarization operating at the highest frequencies, Fig. 2.

Electrical boundary conditions in their limiting cases are determined by the configuration of the elec-

trical circuit with which the electrodes of the polar crystal are in contact.

The first limiting case of electrical boundary conditions corresponds to the case when the polarization is induced *nonelectrically* (thermally, mechanically or optically), and the input resistance of the recording circuit is significantly less than the resistance of the polar crystal itself. Then the crystal can be considered “short-circuited”, and the electric current passing through the input circuit (usually an amplifier) is measured. In this case, it is assumed that the field $E = 0$, i.e., the polar crystal is *electrically free*, and its parameters, for example, permittivity, heat capacity, thermal expansion coefficient, elastic stiffness, etc. are designated as $\varepsilon^E, C^E, \alpha^E, c^E$, etc. Since the electrical induction is equal to $D = \varepsilon_0 E + P$, in an electrically free crystal $D = P$, and therefore the polarization externally induced in the polar crystal generates an electric current: $j_P = dP/dt$, i.e., the crystal is a *source of current*.

The second limiting case of electrical boundary conditions is the case when the polar crystal is *electrically open*, so $D = \varepsilon_0 E + P = 0$; such a crystal is a *voltage source*. When using the static mode to study the crystal, the nonelectrically induced voltage can be measured by an electrometer with a large internal resistance (this is how the Curie brothers discovered the piezoelectric effect). Accordingly, the parameters of the polar crystal are designated as $\varepsilon^D, C^D, \alpha^D, c^D$, etc. The implementation of this condition requires a very low conductivity of the crystal: only in this case the mechanically, thermally or optically induced polarization is completely compensated by the induced electric field: $E = -P/\varepsilon_0$.

When a polar crystal is dynamically excited, the condition $D = 0$ is valid, for example, for lattice waves which have longitudinal polarization (in contrast to the case $E = 0$ when elastic waves in an ionic crystal have transverse polarization). The importance of taking into account the boundary conditions when studying and applying polar crystals and films is due to the fact that, by their physical nature, they are electrothermomechanical energy converters.

2.2. Mechanical properties dependence on electrical state of piezoelectric

From the above equations and Fig. 3 it may be shown that the elastic compliance of an open-circuited piezo-

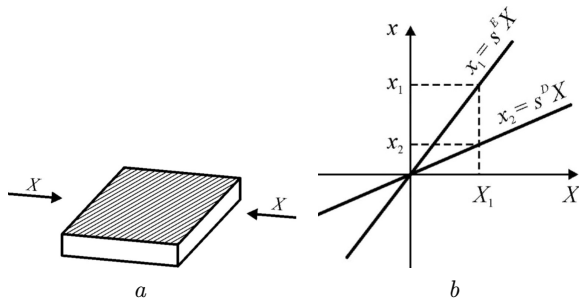


Fig. 3. Difference in elastic compliance of piezoelectric: mechanical action on piezoelectric plate; the shaded area shows the electrode (a); Hooke's law in the cases of open-circuited (s^D) and in short-circuited (s^E) crystal (b)

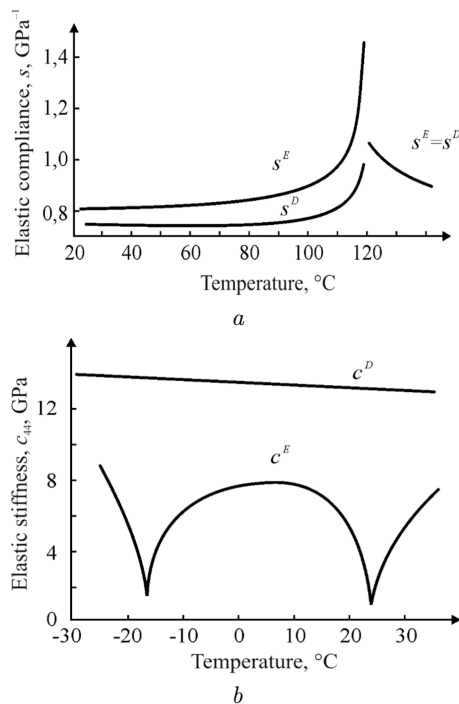


Fig. 4. Effect of electrical conditions on piezoelectric elastic properties: barium titanate elastic compliance: s^D – open-circuited and s^E – short-circuited crystal (a); Rochelle salt elastic stiffness: c^D – open-circuited and c^E – short-circuited crystal [2] (b)

electric crystal s^D should exceed the elastic compliance of a short-circuited piezoelectric crystal s^E .

Indeed, piezoelectricity cannot affect elastic compliance s^E in the short-circuited crystal ($E = 0$). But in the open-circuited case ($D = 0$) the compliance s^D of a piezoelectric plate essentially decreases, Fig. 4, b. In accordance with these designations, the

deformation x can be presented as follows:

$$x = \left(s^E - \frac{d^2}{\varepsilon_0 \varepsilon} \right) X = (s^E - K_{\text{coup}}^2 s^E) X = s^D X;$$

$$s^D = s^E (1 - K_{\text{coup}}),$$

where K_{coup} is the electromechanical coupling coefficient showing what part of the electrical energy is transformed into mechanical energy by a piezoelectric.

Thus, a short-circuited crystal, in which $E = 0$, acts as a piezoelectric “generator of electric current” and, being electrically loaded, for example, by a relatively low input impedance of an amplifying device, has lower mechanical rigidity and, under the action of a certain mechanical stress X_1 applied to it, undergoes a greater mechanical deformation $x = s^E X_1$ than the same crystal, but electrically free with induction $D = 0$, i.e., a piezoelectric “voltage generator”, in which a smaller deformation $x = s^D X_1$ occurs. The reason is that the oriented polar clusters in the electrically free crystal are acted upon by an electric force $E_j = -gX_1$ caused by the direct piezoelectric effect, acting along the polar axis and strengthening the resistance of the clusters to their depolarization (i.e., increasing their “rigidity”).

When a polar crystal is in the open-circuit state, an electric field appears on its surface as a result of the direct piezoelectric effect or the pyroelectric effect, which holds the polar clusters oriented, preventing their free dynamics. At the same time, the role of configurational entropy decreases (as when hydrostatic pressure is applied to the crystal). As a result, elastic compliance s^D is reduced (Figs. 3, b and 4, a) or, equivalently, crystal elastic stiffness is increased, Fig. 4, b.

Experimental evidence of this effect is shown in Fig. 4. In the polar phase of barium titanate (below its ferroelectric phase transition) one can see a large difference between the elastic compliances of the open-circuited and short-circuited crystal. Above the ferroelectric phase transition barium titanate has a cubic centrosymmetric structure and, therefore, the piezoelectric effect is absent; that is why, in the paraelectric phase $s^E = s^D$. Below the phase transition barium titanate turns into a tetragonal polar phase that is characterized by a rather strong piezoelectric effect, so the elastic compliances for various electrical conditions become quite different: $s^E > s^D$. The

elastic compliance s^D decreases most critically at the Curie point.

In the same way, experiments with Rochelle salt, Fig. 4, *b*, show an essential difference in the elastic stiffness c (that is a tensor inverse to the elastic compliance tensor s). The elastic stiffness c is different in the open-circuited and short-circuited cases: $(c_D - c^E)/c_D = K_{\text{coup}}^2$, where K_{coup} is the coefficient of electromechanical coupling. The most impressive difference can be seen at both Curie points of Rochelle salt. These data are obtained by sound velocity measurements, and at the Curie points the sound velocity in Rochelle salt slows down by a factor of 8.

Polar-sensitive structures manifest themselves in crystals as the ability to give an electric (vectorial) response to nonelectric scalar effects (or to more complex tensor-type effects). Hybridized ionic-covalent bonding causes a decrease in the symmetry of the crystal, so polar crystals always belong to noncentrosymmetric classes. Moreover, it is the presence of such bonds that determines the noncentrosymmetric structure of crystals. Therefore, hybridized ionic-covalent bonding is the main cause of pyroelectric and piezoelectric properties. This is based on the asymmetry in the distribution of electronic density along the atomic bonds, which ensures the ability of the crystal to give a polar (electric) response to nonelectric effects.

3. Mechanical Deformation Temperature Dependence

In connection with the discussion of the properties of polar crystals, it is appropriate to give a convincing example showing the direct connection between the thermal expansion coefficient $\alpha(T)$ and spontaneous structural ordering. The ferroelectric barium titanate, when cooling from the high-temperature nonpolar phase, undergoes a phase transition to the polar phase at a temperature of ~ 400 K with a sharp phase and large minimum in the $\alpha(T)$ characteristic. As seen in Fig. 5, *a*, this behavior is typical for ferroelectrics and indicates an increase in their volume during the transition to a polar state. During the phase transition from the disordered paraelectric phase to the ordered polar phase, the volume of the BaTiO₃ crystal increases, and the configurational entropy decreases due to the suppression of polar fluctuations inherent in the disordered paraelectric phase.

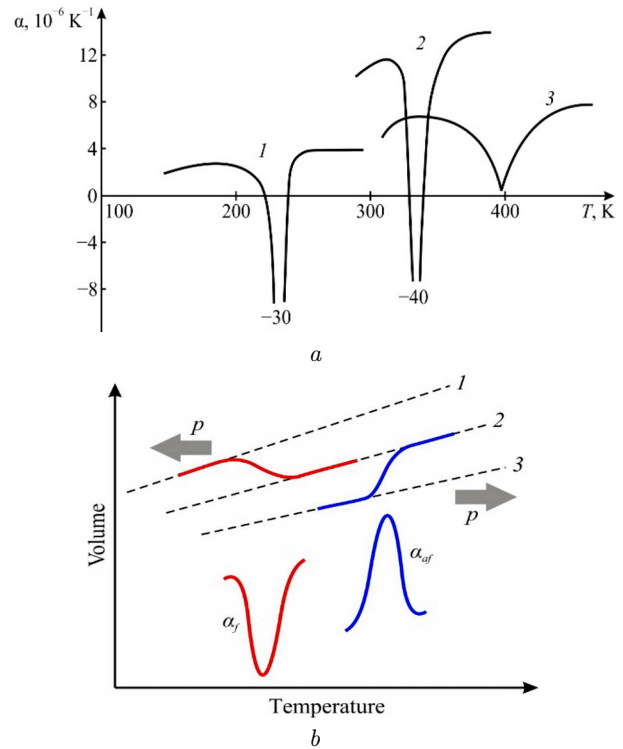


Fig. 5. Mechanical deformation temperature dependence. Thermal expansion coefficient at phase transitions: 1 – KDP = KH_2PO_4 ; 2 – TGS = $(\text{NH}_2\text{CH}_2\text{COOH})_3 \cdot \text{H}_2\text{SO}_4$; 3 – polycrystalline BaTiO₃ (*a*). Anomalies in volume $V(T)$ and $\alpha(T)$ during phase transitions: $2 \Rightarrow 1$ – paraelectric-ferroelectric; $2 \Rightarrow 3$ – paraelectric-antiferroelectric. Designations: 1 – $V(T)$ dependence for polar phase, 2 – $V(T)$ dependence for non-polar phase, 3 – $V(T)$ dependence for antipolar phase, α_f – thermal expansion coefficient at ferroelectric transition, α_{af} – same coefficient at antiferroelectric transition, gray arrows indicate the direction of phase transition temperature T_c displacement with increasing pressure (*b*)

According to measurements, a deep minimum is observed in the $\alpha(T)$ dependence, i.e., negative thermal expansion manifests itself in a certain temperature range, Fig. 5, *a*. Note that similar behavior of the thermal deformation is also characteristic of other ferroelectrics, whereas for antiferroelectrics, an equally large maximum is observed in the $\alpha(T)$ dependence in the region of their phase transitions.

Dynamical structural disordering in BaTiO₃, which has a cubic structure, consists of fluctuations of internal polarity along four [111]-type third-order symmetry axes. The hydrostatic pressure applied to BaTiO₃ below its Curie point (i.e., in its polar phase) returns this crystal to its paraelectric (nonpolar) phase,

in which, naturally, the configurational entropy is larger. Another well-known example of the connection with configurational entropy is the influence of pressure on the phase transition in H_2O at 273 K: the freezing of water leads to ice, which has an increased volume, but externally applied pressure returns the ice to the disordered structure of water possessing more pronounced configurational entropy due to the polar phase fluctuations.

Thus, when discussing negative thermal deformation in polar crystals, one should pay attention to the fact that $\alpha(T)$ takes a negative value in the vicinity of the ferroelectric phase, since the volume of the low-temperature *ordered* phase becomes greater than the volume of the same crystal in its *disordered* phase. However, in the case of the antiferroelectric phase transition, the volume of the antipolar phase, on the contrary, decreases; correspondingly, at the phase transition, the $\alpha(T)$ dependence shows a maximum, Fig. 5, *b*.

In ferroelectrics, the volume of the lower-temperature partially ordered phase becomes greater in comparison with the volume of the higher-temperature disordered paraelectric phase. The hydrostatic pressure, applied to BaTiO_3 below its Curie point (i.e., in the polar phase), returns this crystal into the paraelectric non-polar phase, in which, naturally, the configurational entropy is larger, Fig. 5, *b*. Barium titanate phase transition temperature ($2 \Rightarrow 1$) decreases with increasing pressure at a rate -5 K/kbar [2]; as a result, at the pressure of 30 kbar at room temperature the polar phase in BaTiO_3 already disappears: it is “squeezed out” (in the PbTiO_3 ferroelectric the rate of phase transition temperature decrease is -8 K/kbar [2]). Figure 5, *b* explains symbolically these processes that are completely consistent with the concept of configurational entropy. Naturally, that the increase in volume in the polar phase during ferroelectric transition is accompanied by a minimum of the thermal expansion coefficient.

On the contrary, in the case of antiferroelectrics, the volume of the antipolar phase decreases at the Curie point T_c ; correspondingly, at the phase transition, the $\alpha(T)$ dependence shows a large maximum. As shown in [5], the density of an antiferroelectric does not decrease (as in the case of polar crystals) but it increases, so the entropy in the antipolar phase also decreases. Accordingly, the hydrostatic pressure shifts the Curie temperature T_c to the high-

temperature region, for example, for antiferroelectric PbZrO_3 at a rate of $+5,5$ K/kbar [2].

Uniform pressure, an increase in which suppresses the polar properties of the material and, on the contrary, stabilizes the antipolar phase in agreement with configurational entropy theory.

4. Large Permittivity of Relaxor Ferroelectrics

Large permittivity ε is of great interest in electronics, as it enables the reduction of the size of electronic device components. In conventional dielectrics, their high-frequency permittivity typically is $\varepsilon = 2-10$, whereas in relaxor ferroelectrics and related ferroelectrics with disordered structures exhibiting a diffuse phase transition, the permittivity reaches $\varepsilon = 10^4-10^5$. All these dielectrics are solid solutions of two or more polar dielectrics with a nonuniform distribution of various structural ions. Their high permittivity is observed over a certain temperature range, where intense ordering-disordering of polar clusters occurs near the diffuse phase transition.

It is appropriate to recall that the theoretical limit for the high-frequency permittivity in solids can be estimated as $\varepsilon_{\max} \sim 3 \times 10^5$ [5]. It corresponds, firstly, to the value of $\varepsilon_{\max}$ in some ferroelectrics at their Curie point (where the reorientation of polar clusters is most responsive to a changing electric field), and, secondly, such an instantaneous value of effective permittivity can be achieved while the polarization of ferroelectric domains is switching (from the hysteresis loop it follows that $\varepsilon_{\max} \sim \partial P / \partial E$).

Relaxor ferroelectrics are exceptional examples of ceramics and crystals that exhibit a diffuse phase transition. Their distinguishing feature is the extraordinary “softening” of their dielectric and elastic properties over a broad temperature range.

The crystal lattice of these substances contains “rigid” nanoscale polar formations built into the structure, around which the dynamic polar clusters organize through chaotic thermal motion: this process can occur over a very wide temperature range. Accordingly, the permittivity of relaxor ferroelectrics exhibits a large and broad temperature maximum, at which the giant electrostriction is also observed.

It should be noted that for technical applications of such dielectrics a certain temperature range is required, in which their permittivity is practically ther-

mally stable. Conventional ferroelectrics, such as barium titanate and others, do not meet this requirement: for example, in barium titanate $\varepsilon_{\max} \approx 10000$ is seen only at the Curie point, as well as in strontium titanate $\varepsilon_{\max} \approx 40000$, Fig. 6, curves 3 and 4. That is why, in electronics, high-capacitance miniature capacitors based on ferroelectrics with a diffuse phase transition are used; they have $\varepsilon \leq 10000$ in a temperature interval suitable for technical applications. These are relatively thermally stable ferroelectric ceramics, which consist of many ferroelectric microareas with different phase transition temperatures, which widen the $\varepsilon(T)$ dependence, as shown by curve 2 in Fig. 6. By now, relaxor ferroelectrics have been developed in which $\varepsilon > 50000$, Fig. 6, curve 1. The physical reason for such large permittivity in relaxors is the creation of a structure, in which highly polarizable and rather stable nanoclusters exist, making a great contribution to the permittivity over a broad temperature range.

The technical applications of relaxor ferroelectrics are not limited to subminiature capacitors: they can be applied in nonlinear optical devices (on account of their highly disordered “nonergodic” structure). However, owing to the giant electrostriction, relaxor ferroelectrics are used mainly in nonhysteretic (electrostrictive) actuators in micromechanics. To estimate limitations on the operating speed of relaxor-based electronic devices, the frequency dispersion of permittivity should be studied over a wide frequency range. In this case, it is assumed that the dominant contribution to the permittivity of relaxor materials is the dynamic orientation of polar clusters in accordance with the configurational entropy concept.

In ferroelectrics of displacive type, a sharp peak of permittivity (curves 3 and 4 in Fig. 6) persists over a wide frequency range up to millimeter waves. However, in ferroelectric solid solutions (curve 2) and especially in relaxor ferroelectrics (curve 1 in Fig. 5), the diffuse $\varepsilon(T)$ maximum is seen, decreasing with increasing frequency and shifting to the region of higher temperatures. In relaxor ferroelectrics, this process continues up to the microwave range, Fig. 7.

In relaxor ferroelectrics, the temperature maximum of permittivity was investigated in [8] but at comparatively low frequencies (up to 10^6 – 10^7 Hz). That is why in Fig. 6 the less known microwave $\varepsilon'(T)$ dependence of the PMN crystal is presented [9]. It is obvious that the temperature of the ε' maximum shifts at

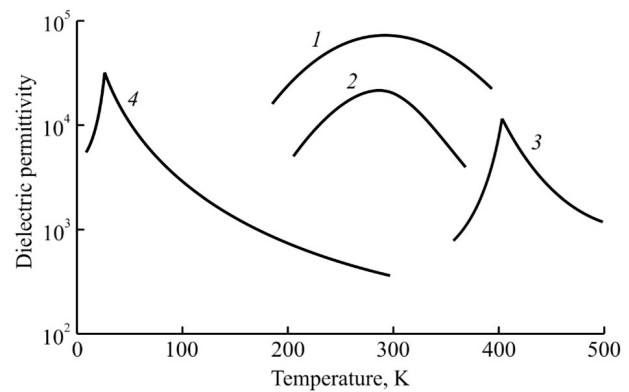


Fig. 6. Permittivity at radio frequencies in dielectrics: relaxor ferroelectric PMN ($\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$) (1), ferroelectric with diffused phase transition $\text{Ba}(\text{Ti},\text{Sn})\text{O}_3$ (2), ferroelectric BaTiO_3 (3), virtual ferroelectric SrTiO_3 (4)

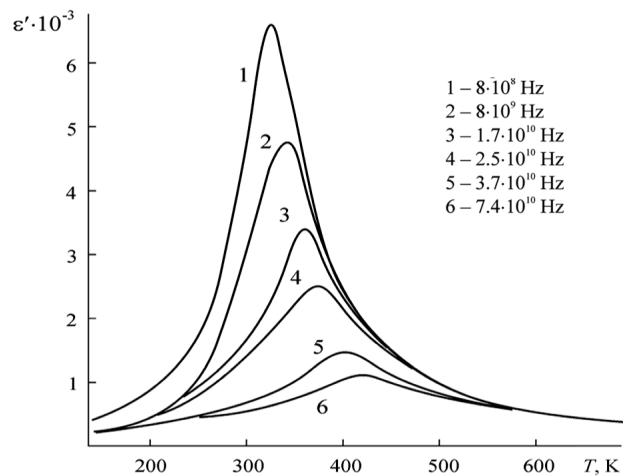


Fig. 7. Temperature dependence of the PMN permittivity at high frequencies

microwave frequencies with increasing frequency. Later it will be shown that at microwaves and at low frequencies the rate of the $T_{\varepsilon'_{\max}}(\nu)$ drift is quite different. The dielectric spectra of relaxor ferroelectrics have been studied in many works, for example in [10, 11], and it has been determined that the dielectric spectra of both PMN crystals and ceramics depend on the relaxation dynamics of the polar nanoclusters. Reorientation and resizing of these clusters in an electric field are considered to be the main mechanisms that manifest themselves in the frequency dependence of the complex dielectric constant. It was also found that thin films of relaxor ferroelectrics show reduced dielectric permittivity at low frequencies, but their high-frequency lattice response is

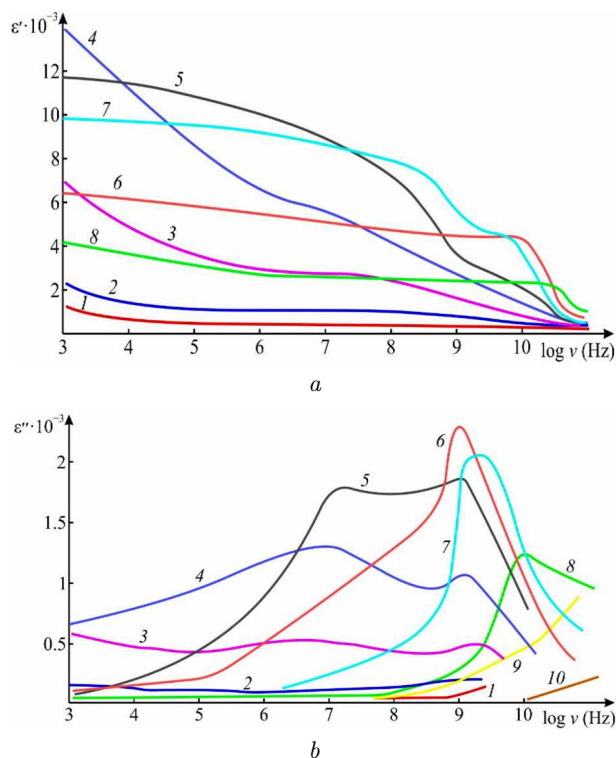


Fig. 8. Dielectric spectra of PMN crystals: permittivity $\epsilon'(\nu)$ (a), loss factor $\epsilon''(\nu)$ at various temperatures (b): 140 K (1), 200 K (2), 240 K (3), 270 K (4), 290 K (5), 300 K (6), 320 K (7), 360 K (8), 400 K (9), 500 K (10)

the same as in single-crystal/ceramic specimens. Research has shown that the lead-free $\text{Ba}_2\text{LaTi}_2\text{Nb}_3\text{O}_{15}$ composition, like PMN, also exhibits the broad maximum of permittivity, characteristic of classic relaxor behavior, with a peak shift from 185 K at 100 Hz to 300 K at 1 GHz. It was also found that broadband dielectric spectroscopy of a PZN-8%PT single crystal demonstrates a stepwise anomaly at $T_c \approx 415$ K that characterizes the ferroelectric phase transition. It is shown that ferroelectric transition (as a rule of first order) is of neither the displacive nor the classical order-disorder type: it reveals a crossover between both types of dynamic behavior. In these materials, at phase transitions, an abrupt increase in the size of the polar clusters, changing below T_C into ferroelectric domains, seems to account for the dynamic manifestation of the ferroelectric transition, without appreciable phonon softening.

To discuss the peculiar properties of relaxor ferroelectric crystals or ceramics using broadband di-

electric spectroscopy, their dielectric spectra should be compared with the spectra of classic ferroelectrics (such as BaTiO_3) and various ferroelectric solid solutions with a diffuse phase transition such as $\text{Ba}(\text{Ti}, \text{Sn})\text{O}_3$, $(\text{Ba}, \text{Sr}, \text{Ca})\text{TiO}_3$, $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ and others. The mentioned materials are also characterized by a broad $\epsilon(T)$ maximum, associated with the random distribution of cations of the same valence in the corresponding sublattices. Composition heterogeneity in the microregions is accompanied by Curie temperature fluctuations that produce a broad $\epsilon(T)$ maximum. However, permittivity in this case practically does not exceed 10^4 . In relaxor ferroelectrics, similar structural sites are occupied by cations of different valences. For example, the lead magnesium niobate crystal ($\text{PMN} = \text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$) has $\text{B}^{+2}\text{--B}^{+5}$ composition disordering; in the quite different case of potassium-lithium tantalate crystal ($\text{KLT} = \text{K}_{1-x}\text{Li}_x\text{TaO}_3$), a disordered structure is created by lithium ions, which are located in the non-central positions with possible associations between them [12].

4.1. Features of PMN and its solid solution

The dielectric spectra of PMN crystals, important for the future discussion, are reproduced in Fig. 8.

When studying dielectric spectra, the concept of complex permittivity is used: $\epsilon^* = \epsilon' - i\epsilon''$ where $\epsilon' = \epsilon'$ and ϵ'' characterizes dielectric losses. The $\epsilon'(\nu)$ dependences at different temperatures demonstrate smoothed changes in permittivity with frequency. The dielectric spectrum is broadened over a wide frequency range (the corresponding data of $\epsilon''(\nu)$ justify this peculiarity).

It can be assumed that the diffuse temperature maximum $\epsilon_{\max}(T)$ in relaxor ferroelectrics is large due to the heterogeneity in the electrical field distribution: the field is applied mostly to “low- ϵ ” microregions (clusters). As a result, the polarizability of these clusters increases and a spatial wave of nonlinear polarization diffuses in the relaxor with the acoustic mode velocity, so strong ϵ -dispersion is seen in this material around the frequency range of $10^3\text{--}10^4$ Hz. However, this motive alone cannot explain the large permittivity peculiar to relaxor ferroelectrics ($\epsilon \sim 10^4\text{--}10^5$) that is observed in a weak electrical field over a broad temperature interval. If the relaxor were a simple composite of low- and high-frequency adjoining polar clusters, the ϵ -value should

be formed predominantly by the clusters that have reduced ε , so the permittivity of relaxor ferroelectrics would not be expected to be so large.

Comparison of relaxor and conventional ferroelectrics of the ABO_3 type is shown in Fig. 9 by the frequency dependence of the temperature maximum of permittivity $T_{\varepsilon'_{\max}}(\log \nu)$ studied in a broad frequency range. Firstly, this characteristic for a typical representative of ferroelectrics, namely barium titanate (denoted as BT in Fig. 9, b), is presented. At the same time, the position of the temperature maximum of permittivity does not depend on the frequency, being determined only by the first-order phase transition. Secondly, to compare relaxor ferroelectrics with other types of weakly ordered ferroelectric *solid solutions* (crystals or ceramics), the dielectric spectra of nonrelaxor but disordered compositions of the ABO_3 type have been studied. Among them, there are *nonlinear* ferroelectric ceramics of $B^{+4}-B^{+4}$ type, whose disordering is due to differences in the B^{+4} ionic radii, for example, in $BSnT = Ba(Ti, Sn)O_3$ compositions, Fig. 9, a. Similar disordering is inherent in *capacitor ceramics* of $A^{+2}-A^{+2}$ type with a very broad distribution of “Curie temperatures” and high $\varepsilon \sim 10^3-10^4$, for instance compositions $(Ba, Sr, Ca)TiO_3$. The fact is that the isovalent replacement of both ions A and B in perovskites does not lead to a violation of charge neutrality in these structures, and therefore the broadening of “phase transition” is due to the random heterogeneity of the above solid solutions. In different microregions of such a composition, the ferroelectric phase transition occurs at different temperatures, resulting in the broad $\varepsilon'(T)$ maximum.

The physical nature of the broad phase transition can be understood from Fig. 9, a for the $BaTiO_3$ – $BaSnO_3$ solid solution used in practice: it corresponds to a mixture of four various phases. Indeed, as the concentration of $BaSnO_3$ increases, the temperature of the $BaTiO_3$ cubic-to-tetragonal ($m3m \rightarrow 4m$) phase transition decreases starting from 400 K while the temperatures of other phase transitions increase: tetragonal–rhombohedral–orthorhombic ($4m \rightarrow 2m \rightarrow 3m$). Near the commonly used composition with 7–12% $BaSnO_3$, four phases can coexist resulting in phase transition broadening.

As can be seen from Fig. 9, b, the temperature of $\varepsilon'_{\max}$ for $BSnT$ shows a gradual increase with frequency. Since a logarithmic scale is used in this figure,

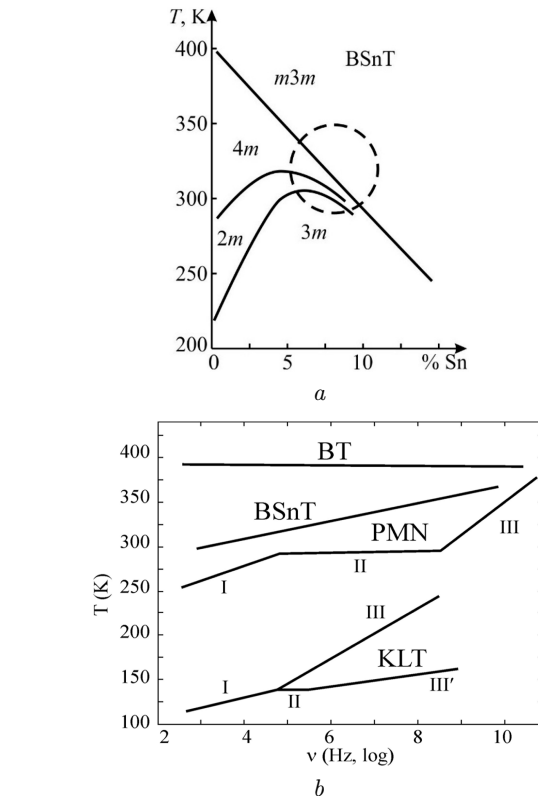


Fig. 9. Ferroelectrics with a diffuse temperature maximum of permittivity: A – phase composition of solid solution $BSnT = Ba(Ti,Sn)O_3$ at different tin concentrations; frequency dependence of ε' -maximum temperature in relaxor ferroelectrics PMN and KLT in comparison with ferroelectric BT = $BaTiO_3$ and solid solution $BSnT$

ure, the rate of $T_{\varepsilon'_{\max}}(\log \nu)$ increase with frequency can be expressed by $\Delta T / \log \nu$ and for $BSnT$ this rate is ~ 7 K. Accordingly, diffuse phase transitions not shown in this figure in PZT and LaPZT, as well as in $Ba(Ti, n, Zr)O_3$ or $(Ba, Sr, Ca)TiO_3$ compositions, also show a linear increase in $T_{\varepsilon'_{\max}}(\log \nu)$ dependence. At the same time, the $BaTiO_3 = BT$ in Fig. 9, b does not change the position of its $\varepsilon'_{\max}$ temperature at the Curie point with frequency: its $T_{\varepsilon'_{\max}} = T_C$, so $\Delta T / \log \nu = 0$. Therefore, ferroelectrics with a diffuse phase transition are characterized by a broadened $\varepsilon'(T)$ peak that is associated with deliberate structural inhomogeneity. Dielectric spectroscopy shows for these materials a linear increase in $T_{\varepsilon'_{\max}}(\log \nu)$.

Therefore, a completely different nature of $T_{\varepsilon'_{\max}}(\log \nu)$ dependence is seen in relaxor ferro-

electrics; for example, for PMN and KLT in Fig. 9, *b*. Typical relaxor ferroelectrics are also ABO₃-type perovskite structure ceramics or crystals, in which the cations of *different valences* randomly occupy similar structural sites. These materials have various types of structural disordering; for instance, their typical representative, the lead magnesium niobate crystal, (PMN = PbMg_{1/3}Nb_{2/3}O₃) has B⁺²–B⁺⁵ composition disordering; another example, the lead iron tungsten solid solution PFW = Pb(Fe_{2/3}W_{1/3})O₃, is characterized by B⁺³–B⁺⁶ structural disordering.

In Section I of Fig. 9, *b*, at relatively low frequencies (approximately up to 10⁵ Hz), the position of a broad $\varepsilon'(T)$ maximum changes with frequency in the same way as in ferroelectric solid compounds and for the same reason: the earlier dispersion of the domain contribution to permittivity. In Section II of Fig. 8, *b*, for PMN-type relaxors, starting from a frequency of $\sim 10^5$ Hz and continuing until $\sim 10^8$ Hz, the position of the $\varepsilon'(T)$ maximum no longer depends on frequency. Only beginning with a frequency near 1 GHz, this maximum begins to shift with frequency toward a higher temperature, Fig. 9, *b*, Section III. In contrast to conventional ferroelectric solid solutions of the ABO₃ type, in the compound PMN = Pb(Mg_{1/3}Nb_{2/3})O₃, electrical neutrality is disturbed in the local nanoregions. In the vicinity of a divalent magnesium ion, a positive electrical charge is formed, which compensates the filled shells of oxygen ions, while a negative electrical charge is formed in the vicinity of pentavalent niobium ions for the same reason. This circumstance stimulates the emergence of polar clusters in the PMN structure, due to which the phase transition significantly broadens, and a unique pliability of such a structure arises, which explains extremely high permittivity, giant electrostriction, and so on.

Dielectric spectroscopy method indicates that in PMN-type relaxors at least two polarization mechanisms dominate. One of them (associated with higher-frequency relaxation) corresponds to Part III of $T_{\varepsilon'_{\max}}(\log \nu)$ dependence in Fig. 9, *b* with the rate $\Delta T/\log \nu = 30$ K, and represents the relaxation dynamics of polar clusters of ~ 10 nm size. This faster polarization is responsible for microwave dielectric dispersion, which takes place in PMN above a temperature of ~ 300 K, where the *superparaelectric phase* exists. Nevertheless, above ~ 650 K (this part is not shown in Fig. 9, *b*), microwave

studies demonstrate a behavior common to paraelectrics. Thus, above a temperature of 650 K, the Curie–Weiss law holds for PMN crystals or ceramics because their superparaelectric state transforms into the usual paraelectric state.

Low-temperature part I of the PMN characteristic in Fig. 9, *b* with the rate $\Delta T/\log \nu \approx 15$ K corresponds to the domain relaxation mechanism in the ferroelectric phase (while cooling, the size of clusters increases, and they transform into small domains). Accordingly, at temperatures lower than 250 K, the audio- and radiofrequency permittivity dispersion (usual for domain polarization) is most essential for PMN. More difficult to interpret is the middle part of $T_{\varepsilon'_{\max}}(\log \nu)$ broken line II with a very low rate $\Delta T/\log \nu \approx 2$ K. The dynamic coexistence of polar and nonpolar clusters can be supposed in this temperature interval. Using dielectric spectroscopy, the relaxation time $\tau(T)$ of these mechanisms and their dielectric contribution $\Delta\varepsilon(T)$ can be separated for study.

In the case of a KLT-type relaxor, Section II in Fig. 9, *b* is narrow, but the $\varepsilon'(T)$ maximum splits into two maxima, the temperature of which gradually increases with increasing frequency, but with a different slope, as shown in Section III. This bifurcation is due to the different nature of polar clusters in the KLT structure, which are stimulated by the dipoles embedded in the structure arising due to the noncentral position of Li⁺¹ ions [12]. There are different polarization mechanisms: one of them is the noninertia lattice polarization that corresponds to the “soft phonon” mode (this mechanism is impossible to show on the limited scales of Fig. 9, *b*). The other two mechanisms correspond to various ways in which mobile Li⁺ ions can move in the multiwell lattice potential (remember that this relaxation occurs in the highly polarizable KTaO₃ “matrix”, and the movement of Li⁺ ions produces in this matrix an *artificial* ferroelectric). One of the relaxation mechanisms, being rather fast, is caused by the thermally activated movement of *individual* Li⁺ ions: the corresponding rate factor in the upper part of the splitting KLT characteristic is $\Delta T/\log \nu \approx 20$ K, Fig. 8, *b*. The other relaxation mechanism, being slower, represents the lower part of the splitting curve (with rate factor $\Delta T/\log \nu \approx 4$ K) and is associated with correlation in the movement of neighboring Li⁺ ions which form polar clusters. While cooling, the increasing intensity of

this movement can transform KLT from a superparaelectric into an “artificial” ferroelectric below 120 K.

Thus, the broadband dielectric spectroscopy method, applied over a wide temperature interval, shows the *relaxor features* of the material very clearly because its $T_{\varepsilon'_{\max}}(\log \nu)$ dependence has a *stepped configuration* (“classic” relaxor ferroelectric PMN is the best example of this feature). There is a good reason to believe that a *broken or bifurcated* $T_{\varepsilon'_{\max}}(\log \nu)$ dependence in relaxors is due to the coexistence of two or more different polarization mechanisms.

Therefore, $T_{\varepsilon'_{\max}}$ frequency dependence demonstrates the following typical situations:

1. Classic ferroelectric of BaTiO₃ (BT) type shows no frequency change in the ε' temperature maximum within the limits of our experimental study (up to 74 GHz).

2. Ordinary ferroelectric solid solutions with diffused phase transition, such as Ba(Ti, Sn)O₃ = BSnT, demonstrate the shift in maximum of $\varepsilon'(T)$ to higher temperatures as frequency increases. The simple explanation of this growing $T_{\varepsilon'_{\max}}$ frequency dependence is the ferroelectric permittivity dispersion due to the domain walls polarization in the polar phase (that is absent in the paraelectric phase).

3. A relaxor ferroelectric shows a broken-line dependence of $T_{\varepsilon'_{\max}}(\log \nu)$. There is a frequency interval (10^5 – 10^8 Hz for PMN) where the position of $T_{\varepsilon'_{\max}}$ practically does not change with frequency (or this change is quite small). Some relaxor ferroelectrics show bifurcation in $T_{\varepsilon'_{\max}}(\log \nu)$ characteristic. An example is KLT, which has two different polarization mechanisms that correspond to various ways in which mobile Li⁺ ions can move in the multiwell lattice potential. There is convincing evidence that in relaxor ferroelectrics two or more types of polar clusters coexist.

4. As follows from the above, the most probable mechanisms of two main dielectric contributions to the diffuse maximum of permittivity are: a low-frequency (1 – 10^5 Hz) contribution to the broad ε -maximum that is usually interpreted as “reorientation of dipole moments of polar nanoregions”. Here it is attributed to strong electromechanical coupling of “soft-polarizable” polar regions, in which electrostriction transforms into the piezoelectric effect. The high-frequency (10^8 – 10^{10} Hz) contribution to the permittivity is commonly explained by the motion of polar nanoregion boundaries. It resembles the microwave disper-

sion of permittivity in ferroelectrics that is due to their multidomain structure, and here it is attributed to “frozen paraelectricity” in the boundaries of polar nanoregions.

Thus, ferroelectrics with a partially disordered structure exhibit a degraded (diffuse) phase transition that is characterized by an extended $\varepsilon(T)$ maximum. With few exceptions, ferroelectrics with a diffuse phase transition are common solid solutions, characterized by nonuniform distribution of the structural ions. An exceptional case among crystals with a diffuse phase transition is the relaxor ferroelectrics, whose distinctive feature is the extraordinary “softening” of their dielectric, elastic, and optical properties over a broad range of temperatures. A peculiarity of the dielectric spectrum of relaxor ferroelectrics is the broken or bifurcated $T_{\varepsilon'_{\max}}(\log \nu)$ dependence; by this feature a relaxor can be distinguished from ordinary ferroelectric solid solutions. The low-frequency mechanism of relaxor permittivity dispersion is attributed to strong electromechanical coupling of “soft-polarizable” polar regions, while the microwave ε -dispersion is due to the “frozen paraelectricity” at the boundaries between polar regions (like in ferroelectric domain walls).

5. Conclusions

The aim of this work is to explain some features of polar crystals, which are widely used in electronics. Polar crystals exhibit a close relationship between their internal polarization and mechanical and thermal properties. It is established that the internal polarity observed in polar crystals arises as structural compensation for the different electronegativity of neighboring ions. In this case, the emerging elementary polar moments, under the influence of thermal motion, combine into dynamically self-organizing polar clusters, determined by the configurational entropy. The resulting structure is very sensitive to any mechanical or thermal effects on the polar crystal. Thus, an increase in hydrostatic pressure suppresses the effect of cluster self-organization by decreasing the configurational entropy. The compression of polar crystals decreases the ferroelectric phase transition temperature; conversely, the temperature of the antiferroelectric transition increases under the influence of hydrostatic pressure, which stabilizes the antipolarity. It is also shown that in relaxor ferroelectrics exhibit-

ing a giant permittivity, an exceptional case of crystals with a diffuse phase transition is observed, whose distinctive feature is the extraordinary “softening” of their dielectric and elastic properties over a wide temperature range.

1. M.E. Lines, A.M. Glass. *Principles and Applications of Ferroelectrics and Related Materials* (Oxford, 2001).
2. J.C. Burfoot, G.W. Taylor. *Polar Dielectrics and Their Application* (Macmillan Press, 1979).
3. S.O. Voronov, V.A. Kazmirenko, Yu.M. Poplavko. Reciprocity of electrical conductance and polarization in their frequency dependence. *Ukr. J. Phys.* **69**, 104 (2024).
4. C. Kittel. *Introduction to Solid State Physics* (John Wiley, 2005).
5. Y.M. Poplavko. *Electronic Materials. Principles and Applied Science* (Elsevier, 2019).
6. Y.M. Poplavko. *Functional Dielectrics in Electronics* (Elsevier, 2021).
7. *Springer Handbook of Materials Data. 2th ed.* Edited by W. Martienssen, H. Warlimont (Springer, 2018).
8. G.A. Smolensky, V.A. Bokov, V.A. Isupov, N.N. Krainik, R.E. Pasinkov, M.S. Shur. *Ferroelectrics and Antiferroelectrics* (Nauka, 1971).
9. Y.M. Poplavko. The nature of large dielectric constant in relaxor ferroelectrics. *Ferroelectrics* **298**, 253 (2004).
10. V. Bovtun, S. Veljko, S. Kamba *et al.* Broad-band dielectric response of $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ relaxor ferroelectric: Single crystals, ceramics and thin films. *J. Euro. Cer. Soc.* **26**, 2867 (2006).
11. V. Bovtun, S. Kamba, S. Veljko *et al.* Relaxor-like behavior of lead-free $\text{Sr}_2\text{LaTi}_2\text{Nb}_3\text{O}_{15}$ ceramics with tetragonal tungsten bronze structure. *J. Appl. Phys.* **101**, 054115 (2007).

12. M.A. Leschenko, Y.M. Poplavko, V.P. Bovtun. Relaxation anomalies in $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$ single crystals. *Ferroelectrics* **131**, 213 (1992).

Received 03.03.26

С.О. Воронов, Ю.М. Поплавко

ЗАСТОСУВАННЯ КОНФІГУРАЦІЙНОЇ ЕНТРОПІЇ ДЛЯ ПОЯСНЕННЯ ОСОБЛИВОСТЕЙ ПОЛЯРНИХ КРИСТАЛІВ

Полярні кристали мають унікальну здатність набувати електричної поляризації під дією неелектричних впливів: механічних, теплових, оптичних та інших. Полярні кристали також здатні здійснювати взаємне перетворення механічної, теплової та електричної енергій, виявляючи п'єзоелектричний і піроелектричний ефекти (як прямі, так і обернені). Електричні параметри полярних кристалів істотно залежать від механічних і теплових умов експерименту і, навпаки, їхні теплові та пружні властивості визначаються електричними умовами. У цій роботі унікальні властивості полярних кристалів аналізуються з використанням експериментальних даних і термодинамічного підходу. Зокрема, власна полярність кристалів пояснюється різницею між електронегативностями сусідніх іонів у кристалічній ґратці, а також самоорганізацією динамічних полярних кластерів, яка пояснюється в рамках поняття конфігураційної ентропії. Ці міркування проілюстровано на кількох прикладах: вплив зовнішніх умов на властивості полярних кристалів, збільшення об'єму полярного стану та висока діелектрична проникність релаксорних сегнетоелектриків.

Ключові слова: полярні кристали, п'єзоелектрики, піроелектрики, сегнетоелектрики, електронегативність, конфігураційна ентропія, релаксорні сегнетоелектрики.