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ELECTRICALLY INDUCED AND CONTROLLABLE PYROELECTRICITY

The main reason for the pyroelectric effect in a polar crystal is that any change in temperature disrupts the established equilibrium between the degree of self-orientation of polar clusters and the intensity of thermal motion in the crystal lattice. This causes thermally induced electric polarization, which is compensated by electric charges that arise on the surface of the pyroelectric material. The conventional pyroelectric effect is only possible in crystals with unidirectional polar symmetry, but another physical mechanism is proposed below, which makes it possible to expand the capabilities of remote temperature measurement. Electrically induced pyroelectricity, maintained and controlled by a bias electric field, is significantly manifested only in paraelectrics and relaxor ferroelectrics, whose high polarizability leads to the appearance of polar clusters. The competition between their ordering under the applied bias field and the disordering effect of thermal motion leads to a thermopolarization effect similar to the primary pyroelectric effect.

Keywords: pyroelectric effect, artificial pyroelectricity, non-polar crystals, paraelectrics, relaxor ferroelectrics.

1. Introduction

The pyroelectric effect has important and diverse applications [1], making the exploration of new materials for its implementation a subject of considerable interest. In addition to the natural pyroelectric effect, the possibility of implementing artificial methods for creating a thermoelectric responses similar to pyroelectricity has been shown, for example, in thin layers of dielectrics, which is promising for their use in the offering promising opportunities for the use in pyroelectric matrix technologies. One of the physical mechanisms that allows the realization of an artificial pyroelectric effect in non-polar materials is described below. It is shown that, in non-polar dielectrics, it is possible to obtain a significant quasi-pyroelectric response that may compete with the traditional pyroelectricity. The method described below uses the electrically induced pyroelectricity in paraelectrics and relaxor ferroelectrics with a high permittivity. It is generally accepted that pyroelectricity is caused by two main mechanisms.

The first of them is explained by a change in the degree of orientation of nano-sized polar complexes under the influence of a chaotic thermal motion in the crystal (more precisely, the influence of this motion on the strength of the dipole-dipole bond of neighboring polar formations). In this case, the cause of the thermoelectric effect in a polar crystal is the disruption of the dynamic equilibrium between the tendency of polar clusters-dipoles to self-orientation and the deorienting effect of the chaotic thermal motion.

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The second mechanism is caused by a thermal deformation of the polar crystal, which is piezoelectrically converted into an electric response. In both cases, the time-varying heat flux required for the registration creates a thermally induced electric polarization in the crystal, which is self-compensated by the generation of electric charges on its surface.

In this paper, a model description of both listed mechanisms is proposed. According to these models, the change in the sign of the pyroelectric coefficient observed at low temperatures can be explained by the change in the sign of the thermal expansion coefficient. This, in turn, is due to the special nature of the interatomic interaction in a polar crystal, which manifests itself below the Debye temperature: in a polar crystal, the nature of the interionic attraction changes. In addition, in this paper, the considerable attention is paid to the tertiary pyroelectric effect and to a new quasi-pyroeffect in piezoelectrics. In this case, the tertiary pyroelectric effect in a piezoelectric is due to a temperature gradient, which is a vector impact. A brief description is also given to the thermoelastic polarization which occurs in the polar-neutral direction of a piezoelectric crystal due to a partial suppression of its thermal deformation.

2. Basics of Pyroelectricity

Pyroelectricity is a thermally induced polarization, which occurs, when the temperature of a polar crystal changes; it is manifested as the appearance of electric charges of different signs on opposite surfaces of the crystal. The reason for thermal polarization is that, in a polar crystal, there is a finely balanced dynamic equilibrium between the level of self-orientation of polar bonds of ionic pairs combined into clusters, and the disordering of this orientation under the influence of the thermal motion. Heating or cooling, affecting the intensity of thermal motion, correspondingly changes the degree of self-orientation of polar clusters, which leads to the appearance of electrical polarization P_i, i.e., to the pyroelectric effect, determinable by the coefficient $\gamma_i = dP_i/dT$, which is a first-rank material tensor, so, its value depends on the orientation of the studied polar crystal.

The main mechanisms of the pyroelectric effect are *primary* and *secondary*, characterized by the pyroelectric coefficients $\gamma_i^{(1)}$ and $\gamma_i^{(2)}$. If the physical conditions of the crystal allow its free deformation, then both effects are summed: $\gamma_i = \gamma_i^{(1)} + \gamma_i^{(2)}$; if thermal deformation is impossible (i.e., the crystal is mechanically clamped), then only the primary pyroelectric effect occurs: $\gamma_i = \gamma_i^{(1)}$. To determine experimentally the coefficient of the secondary pyroelectric effect, it is necessary to compare the data from studies of a free and a clamped crystals: $\gamma_i^{(2)} = \gamma_i - \gamma_i^{(1)}$. Thus, the primary mechanism of pyroelectricity is caused only by internal electrical processes occurring in the pyroelectric, while the secondary mechanism is of electromechanical nature, since it is caused by the direct piezoelectric effect.

Further, it will be shown that both of these effects in non-pyroelectric crystals can be created artificially (which can find application in matrix temperature recording sensors):

- the *primary* pyroelectric effect can be induced by applying an electric bias field, which can find technical application in the non-polar dielectrics possessing high permittivity;
- similar to the *secondary* pyroelectric effect, the effect of thermoelastic polarization can be induced in piezoelectrics in the case of applying special boundary conditions which allow the conversion of a thermal deformation into electricity.

Pyroelectrics belong to an important class of smart dielectrics, since they react very sensitively to changes in the ambient temperature. The pyroelectric effect is a specific property of such polar crystals the structure of which is characterized by the presence of a special (distinguished) unipolar axis. Along it, the self-orientation of polar clusters occurs, and the degree of these partial ordering depends on the temperatvure. That is why such polar structure, when the temperature changes, allows generating an electric signal. This means that, in a pyroelectric, the time-varying thermal energy is partially converted into the electrical energy due to the electrically active internal structure of the pyroelectric.

To understand the features of thermoelectric conversion, it is necessary to analyze known methods that allow us to induce polarity in dielectrics and, thereby, create artificial pyroelectric effects. First, in any solid-crystal (as well as in liquid-crystal), dielectrics, electric polarization occurs, when bending dielectric thin layers [2]. Second, in piezoelectrics, a tertiary pyroelectric effect can occur under the action of a temperature gradient [3]. Thirdly, it has recently been established that, using strain engineering technology, the pyroelectrically active structures can be obtained in thin layers of some dielectrics by creating anisotropic mechanical deformation [4].

However, all these methods, although they are currently of interest for the use in some electronic devices, are still not the topic of this discussion, which is devoted to practically two other problems: the thermoelastic production of artificial pyroelectricity by partially limiting thermal deformations in piezoelectrics [5], and also the electrically induced (and electrically controlled) pyroelectricity in paraelectrics and relaxor ferroelectrics.

In both cases, the research is based on the Curie principle, which takes into account that the symmetry of the state of a crystal under any influence on it contains both the symmetry of the crystal itself and the symmetry of the influence. In the case of mechanically induced pyroelectricity, the thermoelectric response is due to a common element of symmetry between the anisotropic deformation and one of the polar-neutral axes of the crystal, which, in this case, becomes "special". In the case of electrically induced polarity, the biasing polar vector is the electric field, with the result that the resulting thermoelectric response in the dielectric (i.e., "quasi-pyroelectricity") is also described by a vector, just like the usual pyroelectric coefficient.

To explain the nature of artificial pyroelectric effects, it is desirable to briefly consider some features of ordinary pyroelectricity (including those not previously described), while paying attention to the possibility of controlling pyroelectric effects by electrical or mechanical influences.

3. Pyroelectric Effect Modeling

Before discussing the mechanisms of electrically or thermoelastically induced "quasi-pyroelectric" effects, it is appropriate to consider the mechanisms of the ordinary pyroelectric effect, the traditional explanation, which describes it as a change in the spontaneous polarization, is not convincing. In particular, the reason for the frequently observed change in the sign of the pyroelectric coefficient at low temperatures, as well as the impossibility of obtaining the true value of the spontaneous polarization (which can be directly measured only in ferroelectrics), was not explained.

The nature of the spontaneous polarization in pyroelectrics requires clarification, since the ubiquitous free electric charges do not allow the existence of an equilibrium polarized state that is stable over time. A more convincing explanation of pyroelectricity [5] seems to be the assumption that the special electrical properties of non-centrosymmetric ionic crystals are due to hybridized ionic-covalent bonds that activate polarity. In the unexcited state, these bonds do not create an electric field, but they are capable of generating an electrical response to a non-electrical effect, such as a change in heat, pressure, *etc.*

The physical mechanisms of pyroelectricity might be quite complex [6], but, for an explanation of this effect, it is still possible to use a simplified model, which also proves useful for the mechanisms of artificial pyroelectricity discussed below.

3.1. Simplified model of the pyroelectric effect

The pyroelectric effect is an anisotropic phenomenon of the vector type manifesting itself maximally only along a special (unipolar) axis of the crystal. Therefore, the quasi-one-dimensional model considered below seems rational. Both mechanisms of pyroelectricity (primary and secondary) are schematically illustrated in Fig. 1, *a*, which explains the possibility of thermoelectric conversion in a one-dimensional model, which is represented by a chainlet of length l consisting of polar ion pairs.

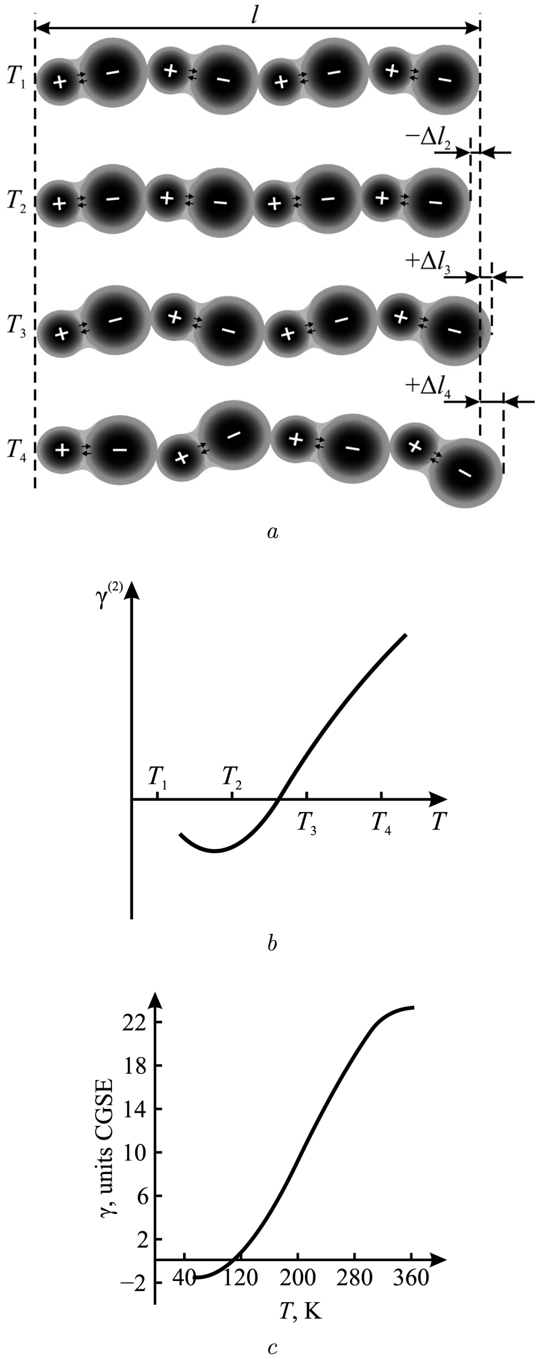
In the initial state of such a conditional 1D polar crystal (i.e., at the lowest possible temperature), the quantum vibrations prevent complete ordering of the polar bonds, which somewhat lengthens the "ideal" crystal lattice by the value Δl_1 (this case is not shown in Fig. 1, *a*, but is included in the specified chain length l). The phenomenon of quantum disordering prevents, for example, the emergence of a polar ferroelectric state in paraelectric crystals of $KTaO_3$ and $SrTiO_3$, in which quantum vibrations prevent the ferroelectric ordering of their structures [5].

Thus, the model presented in Fig. 1, *a* describes the one-dimensional structural organization of polar-sensitive clusters. The change in the model chainlet dimensions with temperature allows us to explain the essence of both main mechanisms of pyroelectricity: the primary effect as a temperature-dependent degree of polar-sensitive bonds' interaction, and the secondary effect as a piezoelectric transformation of thermal expansion-contraction Δl of the polar-sensitive model chainlet.

Note that this simplified model not only describes the usual pyroelectric effect in polar crystals, but also allows us to imagine the mechanisms of electrically and thermo-elastically induced quasi-pyroelectric effects, discussed below. In the first case (non-polar crystal), the emergence of a structure that creates pyroelectricity is induced by an applied electric field. In the second case (in polar-neutral piezoelectricity), one of the directions of spatially compensated polarities is selected from several identical directions, and by creating restrictions on the crystal deformation, only one direction remains allowed for deformation along which thermoelastic polarization occurs, similar to the secondary pyroelectric effect.

As already noted, the polar 1D chainlet shown in Fig. 1, *a* is not considered at almost zero temperature, since its length l depends on the intensity of quantum vibrations of the polar lattice. Let us assume that the temperature, while remaining sufficiently low, increases slightly: in this case, firstly, some disorder in the orientation of the polar pairs is already noticeable, and secondly, the 1D chainlet contracts by the value of $-\Delta l_2$ due to a decrease in the intensity of quantum vibrations. However, with a further increase in the temperature, the usual thermal expansion of the crystal becomes noticeable: first, by $+\Delta l_3$, then by $+\Delta l_4$, etc., which is due to the anharmonicity of the thermal vibrations of the crystal lattice and is described by the thermal expansion coefficient $\alpha \sim T^3$. It is appropriate to note that the negative part of the $\alpha(T)$ dependence indicates a change in the nature of the attractive forces when ions forming the polar bond approach each other [7].

The primary pyroelectric effect, caused by the ordering of polar complexes (which is conventionally shown in Fig. 1, *a* by their small rotations), usually becomes significant above the Debye temperature ($T > \theta_{\mathrm{D}}$), when thermal motion in the crystal lattice becomes quite active. On the contrary, at $T < \theta_{\mathrm{D}}$ (this temperature is usually low, but not always, as in Fig. 1, *c*), the secondary pyroelectric effect prevails, which consists in the piezoelectric transformation of the thermal deformation of the lattice, which is obviously possible only in a free deformable crystal.



a

b

c

Fig. 1. One-dimensional model of pyroelectricity: chainlet of connected ions, where shaded areas approximately indicate electron density distribution in outer shells, the volume of negative ions is larger, since they contain valence electrons (*a*); expected temperature dependence of the secondary pyroelectric coefficient (*b*); pyroelectric coefficient temperature dependence in the lithium sulfate crystal $Li_2SO_4 \cdot H_2O$ [6] (*c*)

3.2. The secondary pyroelectric effect

It is obvious that the 1D model presented in Fig. 1, *a* also describes the piezoelectric properties, thereby successfully explaining the secondary pyroelectric effect as a piezoelectric transformation of the temperature deformations of the polar crystal. Both mechanical stretching and compression of the 1D chainlet lead to a change in its electric moment: $\Delta M^{(2)} \sim \pm\Delta l/l$. The proportionality of the electric moment $\Delta M^{(2)}$ to the temperature increment Δl follows from the linear dependence of a thermal deformation on temperature: $\Delta l \sim \alpha\Delta T$, where α is the coefficient of thermal expansion.

In the general case, this determines the linear dependence of the mechanically induced electric moment on the deformation

$$\Delta M^{(2)} \sim e\Delta l/l, \qquad (1)$$

where e is the piezoelectric deformation constant. It is an anisotropic parameter, the value of which is given in reference books, and can also be calculated through the corresponding piezoelectric modulus d and the elastic constant c: $e = d \cdot c$ (this entry is simplified, actually in the tensor representation $e_{im} = d_{in}c_{mn}$ where $i = 1, 2, 3$ and $m, n = 1, 2, ..., 6$). From the above linear equation it follows that $\Delta M^{(2)} \sim \gamma^{(2)}\Delta T$, where the coefficient $\gamma^{(2)} = e \cdot \alpha$ is the piezoelectrically transformed thermal deformation. Naturally, the dependence $\gamma^{(2)}(T)$ corresponds to the temperature dependence of the thermal expansion coefficient $\alpha(T)$ (Fig. 1, *b*). It is seen that in polar crystals this coefficient initially (at low temperatures) has a negative value, and only then increases according to the usual law, when $\gamma^{(2)} \sim \alpha \sim T^3$.

An example of the $\gamma^{(2)}(T)$ dependences in a pyroelectric crystal is shown in Fig. 1, *c*. It is noteworthy that, at low temperatures, the pyroelectric coefficient tends to decrease down to a negative value. It is interesting to note that many pyroelectric crystals, for example the pyroelectric symmetry semiconductors of the $\mathrm{A^{II}B^{VI}}$ group (such as CdS), also demonstrate a change in the sign of the pyroelectric coefficient at low temperatures. It should be noted that this phenomenon is not consistent with traditional ideas about spontaneous polarization. Partly for this reason it is assumed that, in non-centrosymmetric crystals, the internal polarity arises due to structural compensation of the interaction of neighboring atoms with different electronegativity.

3.3. Prerequisites for obtaining artificial secondary pyroelectric effect

In connection with the discussion of the secondary pyroelectric effect, it is appropriate to note that piezotransformed thermal deformation can also cause another similar effect, which is observed not only in polar pyroelectric crystals (mentioned above), but also in polar-neutral piezoelectric crystals. Thus, in piezoelectrics, a significant thermoelectric response (analogous to the pyroelectric effect) can be obtained in two ways:

- by creating unique boundary conditions in the piezoelectric, providing a quasi-pyroelectric response, if the thermal influence on the crystal is uniform [5];
- under the influence of a temperature gradient, which is a non-uniform (vector) effect on the crystal [3].

3.4. The tertiary pyroelectric effect

In non-pyroelectric piezoelectrics, a uniform (scalar) change in temperature, as well as a comprehensive (hydraulic) change in pressure, does not lead to any electrical response. However, an effect similar to the secondary pyroelectric effect can be created in the polar section of a piezoelectric by a temperature gradient (i.e., by a vector-type effect). Such a tertiary pyroelectric effect is initiated in a piezoelectric by directional thermal deformation. The tertiary pyroelectric effect has low inertia, so it can be useful when measuring short high-power laser pulses or for measuring high-power microwave radiation.

Thus, unlike the primary and secondary pyroelectric effects, which arise due to a time-varying spatially homogeneous temperature impact, the tertiary effect is generated by the influence of a temperature gradient (also dynamically changing in time). The physical nature of the tertiary pyroelectric effect is very close to the secondary pyroelectric effect, since both are caused by thermal deformation directed along one of the polar directions of the crystal. Under the influence of the vector (the temperature gradient), one of the polar-neutral axes of the piezoelectric becomes a special (as if "pyroelectric") polar axis in accordance with the Curie principle.

In the original studies, the induced by temperature gradient thermoelectric effect was observed in quartz crystal and was called actinoelectricity; only now it is interpreted as tertiary pyroelectricity [3]. The temperature change of the intrinsic polar moment of a piezoelectric caused by thermal stress is simply defined as: $M^{(3)} = d \cdot c \cdot \alpha$, where d is the piezoelectric modulus, c is the elastic stiffness, and α is the

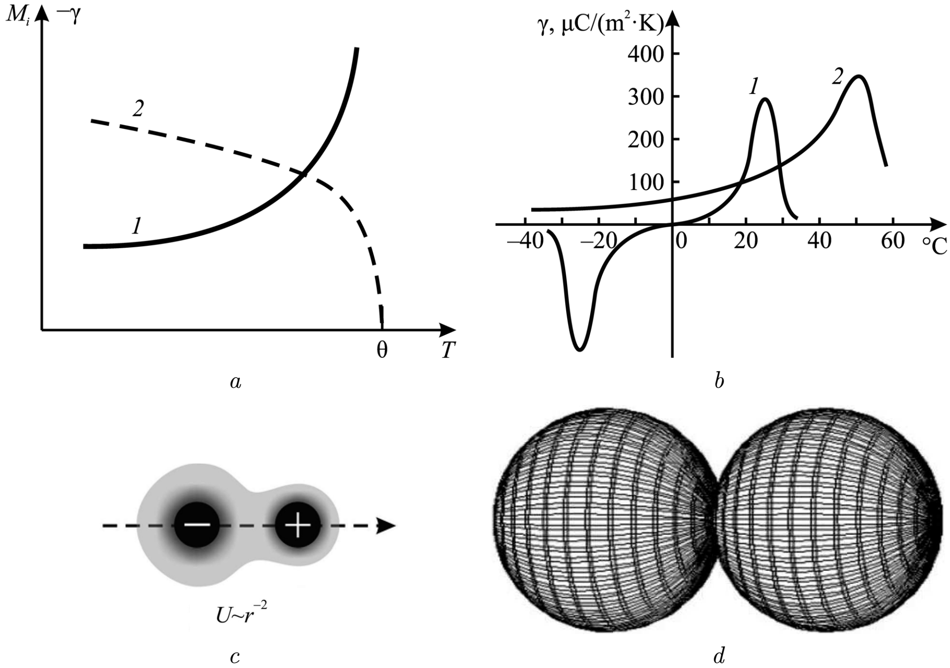


Fig. 2. Primary pyroelectric effect: interdependence of pyroelectric coefficient (*1*) and internal polarity moment (*2*) (*a*); pyroelectric coefficient in typical ferroelectrics: *1* – Rochelle salt ($KNaC_4H_4O_6{\cdot}4H_2O$); *2* – triglycine sulfate $(NH_2CH_2COOH)_3{\cdot}H_2SO_4$ (*b*); dipole modeling of pyroelectricity (*c*); indicatrix characterizing spatial distribution of pyroelectric coefficient for primary pyroelectric effect (*d*)

coefficient of thermal expansion [4]. The tertiary pyroelectric effect can also be defined as a temperature change in the polarization of a piezoelectric caused by thermal stress. A uniform temperature change in a mechanically free crystal cannot lead to an electrical response, since the crystal is uniformly deformed and stresses do not arise in it. Nevertheless, it will be shown below that even with uniform thermal excitation of the piezoelectric (when grad $T = 0$), a polar response can be obtained, when necessary conditions are created that eliminate some of the thermal deformations.

3.5. The primary pyroelectric effect

As the temperature increases, the chaotic thermal motion partially disrupts the self-orientation of polar nanoclusters (Fig. 1, *a*), but their dipole-dipole interaction tends to maintain their orientation, preventing the disordering of polar clusters, that determines their resistance to an increase in thermal disorder. In most pyroelectrics, this mechanism is maintained until the polar crystal melts, but in ferroelectrics (which are a special case of pyroelectrics), thermal motion still leads to complete disordering of polar clusters, and a phase transition of the crystal to a non-polar phase at the Curie point.

In ferroelectrics, the thermally dependent competitive orientation-disorientation process can also be influenced by an external electric field, which promotes a stronger ordering of clusters and thereby affects the pyroelectric response, controlling its magnitude. Thus, the weakening or strengthening of the polar structure stability depends both on the intensity of thermal motion and on the magnitude of the applied field.

When describing the mechanism of the primary pyroelectric effect shown in Fig. 1, *a*, it should be noted that the elementary electric polar moment dm arising when temperature changes is proportional to the variation in the energy of thermal motion: $dm \sim k_{\rm B}T$, where $k_{\rm B}$ is the Boltzmann constant. The elementary moments of the 1D model chainlet are summed up: $M^{(1)} \sim \gamma^{(1)}\Delta T$, where ΔT is the temperature range, $\gamma^{(1)}$ is the coefficient of the primary pyroelectric effect, Fig. 2, *a*. It should be noted that “more strongly self-oriented” polar bonds react more weakly to a change in temperature than "more pliable" polar clusters. For this reason, the primary pyroelectric coefficient $\gamma^{(1)}$ of "more stable" pyroelectrics is significantly lower than that of "more pliable" ones. The latter include ferroelectrics and related materials, in which chaotic thermal motion more easily disrupts the self-correlation of nanosized polar clusters, that is especially evident near the phase transition.

Figure 2, *b* shows the temperature dependence of the pyroelectric coefficients of two well-studied ferroelectrics: triglycine sulfate (TGS) and Rochelle salt (RS). In the first of them, its pyroelectric coefficient is very high ($\gamma^{(1)} \sim 350\ \mu Q/(m^2K)$), exceeding most known pyroelectrics, while the theoretical description of the properties of TGS is in full agreement with Landau's theory. In addition, the temperature maximum of the pyroelectric coefficient $\gamma^{(1)}(T)$ in TGS crystals is observed in the region of normal temperatures, which is very important for its use as temperature sensors.

Rochelle salt is an interesting object not only because it is a crystal, in which ferroelectricity was first discovered, but also because it has two Curie points: ferroelectric (+24 °C) and antiferroelectric (−18°C). It is noteworthy that, in the RS crystal, the sign of its pyroelectric coefficient changes, which indicates, firstly, that in the RS crystal at temperature (−18 °C) changes the symmetry, and, secondly, the fact that it is not ferroelectric domains that are responsible for pyroelectricity, but the nano-sized polar clusters, which are very responsive even to small influences.

The primary pyroelectric effect is maximal along one (selected) polar axis of the crystal, and such a one-dimensional case can be modeled by a dipole, Fig. 2, *c*, whose energy decreases with distance as $U \sim r^{-2}$. The piezoelectric coefficient is characterized by a material vector (first-rank tensor): $\gamma_i(\varphi) = \gamma_{i\ \max} \cdot \cos\varphi$, where φ is the angle between the polar direction and the oblique cut of the crystal on which the piezoelectric effect is studied. Its indicatory surface, shown in Fig. 2, *d*, consists of two spheres located left and right of the symmetry plane.

From the above, it follows that two main mechanisms make it possible to obtain pyroelectricity as the thermally induced polarization: $\Delta M \sim (\gamma^{(1)} + \gamma^{(2)})\Delta T$. At that, in the linear ("hard") pyroelectrics (such as lithium sulfate, tourmaline, zinc oxide, etc.), the pyroelectricity is predominantly due to the secondary effect (piezoelectrically converted thermal deformation). In this case, the reason for this transformation is the rigidly organized internal polar-sensitive structure inherent in all piezoelectrics. It is obvious that this fundamental mechanism cannot be significantly controlled by an external electric field up to the breakdown voltage. However, in the "soft" (nonlinear) pyroelectrics, which are predominantly ferroelectrics and related materials, pyroelectricity is caused by a violation of the delicate balance in the equilibrium between the self-orientation of polar clusters and disordered thermal motion. With this mechanism (i.e., the primary pyroelectric effect), the change in polar sensitivity with temperature is described by the equation $\Delta M^{(1)} \sim (\theta - T)^{0.5}$, where θ is the Curie–Weiss temperature, and the degree "0.5" is the critical Landau index. This makes it possible to realize an electrically induced quasi-pyroelectric effect in such materials.

3.6. Prerequisites for obtaining artificial primary piezoelectric effect

In connection with the description of the primary mechanism of pyroelectricity, it should be noted that the electric polarization is related to the electric field as $P = \varepsilon_0\chi E = \varepsilon_0(\varepsilon - 1)E$, where ε_0 is the electrical constant, $\chi = \varepsilon - 1$ and ε is the relative permittivity. For $\varepsilon \gg 1$, the pyroelectric coefficient can be defined as $\gamma \approx \varepsilon_0(d\varepsilon/dT)E$. It follows that the permittivity is related to the pyroelectric coefficient; moreover, the pyroelectric coefficient is proportional to the temperature coefficient of permittivity: $TC\varepsilon = \varepsilon^{-1}(d\varepsilon/dT)$. In most ionic and covalent crystals, the permittivity is small ($\varepsilon \leq 10$) and weakly depends on both temperature and electric field. Therefore, only a very weak "quasi-pyroelectric" response can be induced in them by an electric field.

On the contrary, the ferroelectrics and related crystals are a completely different case, since their permittivity is very high ($\varepsilon \sim 10^3 \times 10^4$). Moreover, in this case, the permittivity varies greatly with temperature and it is dependent on the electric field. Therefore, it is the ferroelectrics and related materials that look like very promising objects for the use of electrically induced and electrically controlled artificial pyroelectricity.

4. Artificial Pyroelectricity

Pyroelectrics that use the temperature dependence of the naturally existing polarization of crystals (as in Fig. 2) are widely used in both single and matrix temperature sensors [1]. However, it is of sizable interest to expand the possibilities of obtaining such sensors. In particular, they would be based on the temperature change of electric polarization created and maintained by an external electric field. At that, it is necessary to use dielectrics with a very high permittivity: only in this case, the artificially induced pyroelectricity becomes large enough to compete with known pyroelectrics. The need to apply an external bias field is an obvious disadvantage of such sensors, but per contra, this field allows electrical control over the sensitivity of the matrix sensor, and gives the opportunity to compensate for possible changes in the operating temperature. At the same time, the range of materials that can be used in thermal sensors is significantly expanded, mainly due to the use of paraelectrics and relaxor ferroelectrics.

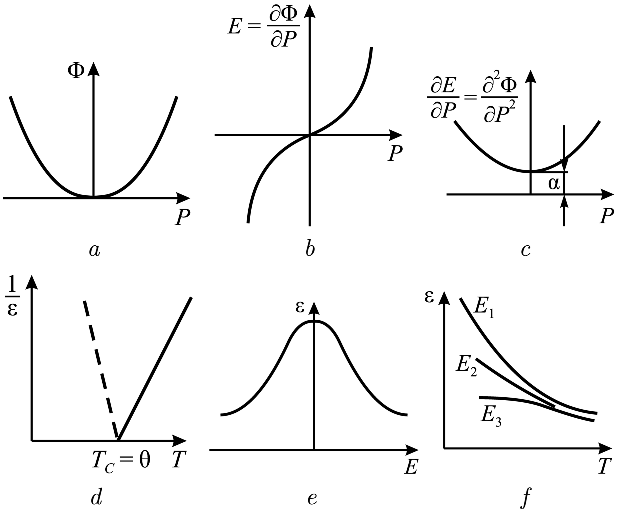


Fig. 3. Landau theory: dependences of thermodynamic potential (*a*) and its derivatives (*b*, *c*) on the ordering parameter P above T_C; temperature dependence of the inverse permittivity (*d*), dielectric nonlinearity (*e*); permittivity in non-polar phase at different control fields $E_1 < E_2 < E_3$ (*f*)

To analyze the artificial pyroelectric effect induced in paraelectrics, it makes sense to apply the theory of Landau phase transitions, which allows one to determine the pyroelectric coefficient of ferroelectric crystals

$$\gamma = \frac{dP}{dT} = \varepsilon_0 E \frac{d(\varepsilon - 1)}{dT}. \tag{2}$$

To describe the thermoelectric properties of ferroelectrics that have a second-order phase transition, one can use the expansion of the free energy Φ in a series in terms of the fluctuating polarization P, Fig. 3, *a*, which, in the Landau theory, takes a polynomial form:

$$\Phi(T, P) = \Phi_0(T) + \frac{\alpha}{2} P^2 + \frac{\beta}{4} P^4, \tag{3}$$

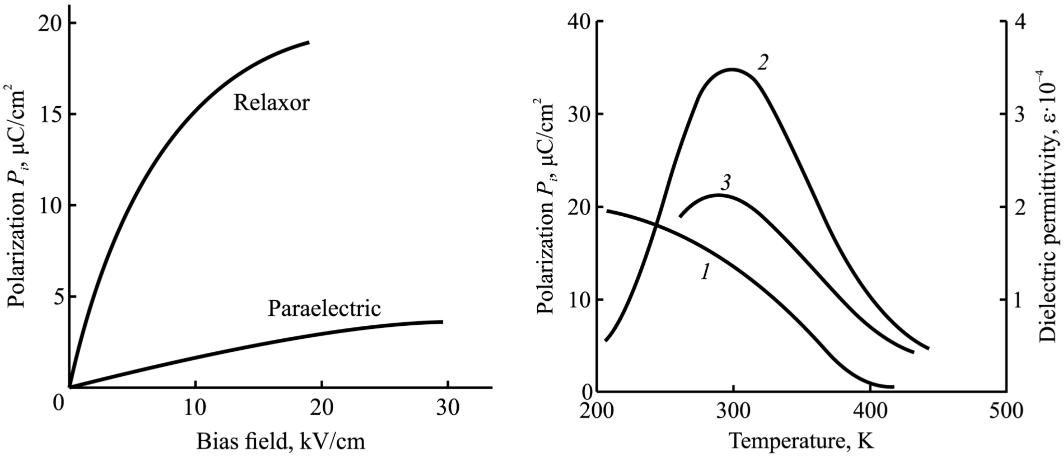
where the first term Landau is $\alpha = \alpha_0(T - \theta)$ and $\beta > 0$ is the second term which should be positive to maintain lattice stability. Considering that the electric field can be defined as a derivative $\partial\Phi/\partial P$, Fig. 3, *b*, the above expression can be rewritten as: $E = \alpha P + \beta P^3$. From this the dielectric susceptibility χ can be found:

$$\chi^{-1} = \frac{\partial E}{\partial P} = \alpha + \beta P^2 \tag{4}$$

(Fig. 3, *c*). In this given case, it is possible to consider that $\chi \approx \varepsilon$, since $\varepsilon = 1 + \chi$ and permittivity of ferroelectrics is very large ($\varepsilon \gg 1$), so $\varepsilon^{-1} = \alpha + \beta P^2$. For electrically induced artificial pyroelectricity, a nonpolar (paraelectric) phase is used, described by the Landau theory for the case, in which the first term in the above polynomial is positive: $\alpha > 0$. Thus, the paraelectric phase of the ferroelectric is considered, located above the phase transition temperature: $T > T_C$, Fig. 3, *d*. In this case, the phase stability conditions are: $\partial\Phi/\partial P = 0$ and $\partial^2\Phi/\partial P^2 > 0$. The first of these expressions can be reduced to the cubic equation $\alpha P + \beta P^3 = 0$, which can have only one real root $P_1 = 0$, since the order parameter is polarization, and above T_C the high-temperature phase is disordered.

Next, consider the temperature dependence of the permittivity above the Curie point, Fig. 3, *d*, which follows from the above formulas and is a Curie–Weiss law: $\varepsilon^{-1} = \alpha_0(T - \theta)$ or $\varepsilon = C(T - \theta)^{-1}$, where C is the Curie–Weiss constant. At that, permittivity depends not only on temperature but also on the strength of the electric field, Fig. 3, *f*. From the above expressions, it follows that, in the paraelectric phase, a significant dielectric nonlinearity should be observed, Fig. 3, *e*. The point is that $P(E)$ dependence is characterized by a saturation area, Fig. 3, *b*, so the permittivity $\varepsilon \sim \partial P/\partial E$ in paraelectrics decreases in a strong electrical field. General formula [5], which involves both ε-nonlinearity and its temperature dependence in the paraelectric phase is:

$$\varepsilon(T, E) = \frac{C}{T - \theta} \left[1 + 3\beta\varepsilon_0^3 E^2 \frac{C^3}{(T - \theta)^3} \right]^{-\frac{1}{3}}. \tag{5}$$



a *b*

Fig. 4. Relaxor ferroelectric characteristics: comparison of electrically induced polarization P_i in PMN with paraelectric BST (*a*); PMN properties (*b*): *1* – polarization P_i induced by 10 kV/cm; *2* – permittivity at $E_{\text{bias}} = 0$; *3* – permittivity at $E_{\text{bias}} = 10$ kV/cm

It is evident that, in the non-polar phase, the closer the paraelectric temperature is to the phase transition temperature, the higher the dielectric nonlinearity. Moreover, the more the permittivity depends on temperature, the stronger the dependence $\varepsilon(T)$ and, therefore, the higher the artificial "pyroelectric" coefficient. This means that the highest value of the induced pyroelectric effect can be observed near the Curie–Weiss temperature; this happens because the closer the temperature is to the Curie point, the steeper the dependence of the permittivity on temperature. Moreover, the value of such "pyroelectricity" becomes greater, when the second Landau coefficient β is reduced in the material, i.e., when the long-range forces in the crystal lattice that ensure the stability of the polar crystal are weakened.

It should be noted that a steep slope of the dependence $\varepsilon(T)$ also implies increased permittivity, which reduces the integral sensitivity of pyroelectric sensors. Therefore, when choosing a material for a pyroelectric sensor, it is necessary to search for compromise solutions. Indeed, the very high permittivity in relaxing ferroelectrics ($\varepsilon_{\max} \sim 5 \times 10^4$) may not correspond to the condition of very large permittivity due to the blurring of their phase transition, since the $\varepsilon(T)$ dependence in them is smoother. However, in the paraelectric phase of usual ferroelectrics, at the phase transition temperature ($T \approx \theta$, i.e., Curie point) their permittivity reaches $\varepsilon \sim 5 \times 10^3$, and their paraelectric phase (at a temperature $T > \theta$) might be more promising for application in sensors, so, it does not contain thermally unstable domains in the critical region. Moreover, for some paraelectrics the second Landau coefficient β might be smaller due to weak long-range interactions in the crystal lattice.

To assess the possibilities of using the above main classes of materials in dynamic thermal sensors, we have comparedon the induced polarization in the relaxing ferroelectric $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ = PMN with the similar polarization of the paraelectric material $\text{Ba}(\text{Ti}_{0.6}\text{Sr}_{0.4})\text{O}_3$ = BST shown in Fig. 4, *a*. It can be seen that the electrically induced polarization in PMN is significantly greater than in BST: the reason is that relaxing ferroelectrics have a much higher dielectric permittivity. As in the conventional ferroelectrics, in the relaxing ferroelectrics their polarization depends on the temperature, Fig. 4, *b*. For technical purposes, it is important that in a biasing electric field, a relaxor ferroelectric exhibits an electrically induced pyroelectric effect, the magnitude of which is comparable to the pyroelectric coefficient of a conventional pyroelectric. At the same time, compared to the induced pyroelectric effect observed in BST-type paraelectrics, the induced pyroelectric effect in PMN is more thermally stable due to the lower slope of the $P_i(T)$ dependence.

The physical mechanism for producing artificial pyroelectricity in paraelectrics is illustrated in Fig. 5, which shows the temperature dependence of the internal (non-induced) polarization varying with temperature $P(T) \sim (\theta - T)^{0.5}$ where 0.5 is the critical Landau index. As already noted, it is in this case that the $P_i(T)$ dependence is used, which makes it possible to obtain the primary pyroelectric effect, as in Fig. 2, *a*.

The solid line in Fig. 5, *a* shows the polarization induced by an applied electric field, which shifts the phase transition to higher temperature. An electric displacement (bias) field E_b at a given temperature T_b creates a "working region", in which the induced polarization is equal to P_b (without an electric displacement field, this non-polar region cannot exhibit a pyroelectric effect). It should be noted that the bias electric field, displacing the phase transition, not only induces a polar phase instead of the paraelectric phase, but also makes it possible to regulate the sensitivity of the "pyroelectric element" and can also compensate for the influence of changing external conditions on its operation.

In the working region created by the displacement field, a change in the temperature of the paraelectric by an amount of $+\delta T$ (or by $-\delta T$) leads to a corresponding change in the induced polarization ($+\delta P$ or $-\delta P$), which, in turn, causes the appearance of a changing pyroelectric current.

The role of the electric field E_b is that it maintains the induced polarization of E_b and resists the temperature decay of the artificially created polar structure. This equilibrium is disturbed by the external heating or cooling; but due to the change in temperature, a new equilibrium is established, which is accompanied by a change in polarization, which is detected by the induced pyroelectric current supplied to the amplifying transistor.

It should be noted that the mechanism for the occurrence of an artificial pyroelectric effect in a paraelectric can be described in another way, Fig. 5, *b*. In an electric field applied to a ferroelectric, the phase transition and the dielectric permittivity maximum shifts towards higher temperatures and, at the same time, expands somewhat. In the operating region induced by the control electric field (centered at point E_b, which corresponds to the base temperature T_b), the pyroelectric capacitor-sensor has a base capacitance C_b corresponding to the dielectric permittivity ε_b, and contains a field-induced electric charge: $Q_b \sim C_b$.

If the temperature of such a capacitor-sensor increases by $+\delta T$, its capacity will decrease by δC; in this case, an excess charge $-\delta Q_b$ occurs, which flows in the input circuit of the amplifier, indicating an electrical signal about an increase in temperature. On the contrary, when the temperature decreases by $-\delta T$, the capacitance of such a sensor increases and is charged by the magnetizing field with an additional charge $+\delta Q_b$, which is also detected by an electrical signal, but of the opposite sign.

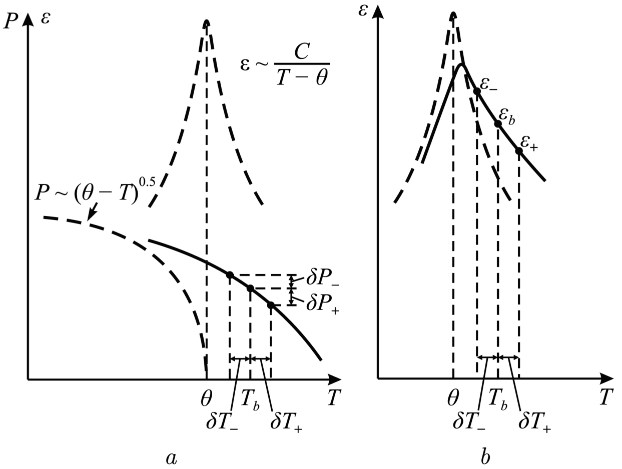


Fig. 5. Artificial pyroelectric effect induced by bias field in the paraelectric phase of a ferroelectric: temperature dependence of the ferroelectric's permittivity ε and polarization P without electric field (dotted line) and under applied bias electric field (solid line) (*a*); permittivity without bias field (dotted line) and under bias electric field (solid line) (*b*)

Induced by the electric field artificial pyroelectric effect in paraelectric ceramics finds application in the matrix infrared image sensors. The pyroelectric sensitive matrix is manufactured using hybrid microelectronics methods, and contains many identical elements, each of them is equipped with a separate transistor amplifier. As to the paraelectric, it is advisable to use exactly paraelectric ceramics, in which it is easier, than in a crystal, to ensure complete uniformity of miniature sensing elements. The controlling electric field provides the pyroelectric properties of all elements by applying an electric bias field that induces and maintains the pyroelectric effect. Pyroelectrics are used not only in pyroelectric vidicons, but also in high-sensitivity pyrometry, in motion detectors, infrared thermometers, *etc.*

5. Conclusions

The reason for thermally induced polarization is that, in pyroelectrics, a finely balanced dynamic equilibrium exists between the level of self-orientation of polar bonds of ionic pairs combined into clusters and the disordering of this orientation under the influence of the thermal motion. In addition to polar crystals, the quasi-pyroelectric effect can be obtained in nonpolar crystals by creating an induced polarity in them through applying an external electric field. This effect can be comparable with the natural pyroelectric effect in dielectrics with very high permittivity, which finds applications in integral matrix temperature sensors. The article investigates various mechanisms of the thermoelectric effect in dielectrics and proposes models that explain the main phenomena, including the change in the sign of the pyroelectric coefficient at low temperatures. The mechanisms for obtaining the electrically induced pyroelectric effect in paraelectrics and relaxor ferroelectrics are described.

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ЕЛЕКТРИЧНО ІНДУКОВАНА ТА КЕРОВАНА ПІРОЕЛЕКТРИКА

Основною причиною піроелектричного ефекту в полярному кристалі є те, що будь-яка зміна температури порушує встановлену рівновагу між ступенем самоорієнтації полярних кластерів та інтенсивністю теплового руху в кристалічній ґратці. Це спричиняє термічно індуковану електричну поляризацію, яка компенсується електричними зарядами, що утворюються на поверхні піроелектричного матеріалу. Звичайний піроелектричний ефект можливий лише в кристалах з односторонньою полярною симетрією. У статті запропоновано інший фізичний механізм, що дає змогу розширити можливості дистанційного вимірювання температури. Електрично індукована піроелектрика, яка підтримується та контролюється зовнішнім електричним полем, значною мірою проявляється лише в параелектриках і сегнетоелектриках-релаксорах, висока поляризованість яких приводить до утворення полярних кластерів. Конкуренція між їх впорядкуванням під дією прикладеного електричного поля та дезорієнтувальним ефектом теплового руху приводить до термополяризаційного ефекту, подібного до первинного піроелектричного ефекту.

Ключові слова: піроелектричний ефект, штучна піроелектрика, неполярні кристали, параелектрики, сегнетоелектрики-релаксори.