SYMMETRY ANALYSIS OF INDUCED PYROACTIVITY IN RADIALLY INHOMOGENEOUS TEMPERATURE FIELDS

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For the first time, a symmetry approach to studying the induced pyroactivity in acentric crystals under thermodynamically nonequilibrium conditions is advanced. Symmetry analysis of the properties of polar states is performed, and all possible types of pyroactive crystallographic cuts are determined in each of twenty piezoelectric classes in radially inhomogeneous temperature fields. It is shown that the tertiary pyroelectric effect can manifest itself in both polar and nonpolar crystallographic cuts. In the general case, the induced polarization vector is not coincident with the sole polar direction which is contained in the group describing a crystal symmetry in the external field. The results of the symmetry analysis agree with the experimental data which have been first explained on its basis. The elaborated symmetry approach turns out to be an efficient method for revealing the peculiar properties of a spatial polarization distribution. This information is required for developing the physical foundations of a new class of sensor devices operating on the basis of the induced pyroactivity in acentric crystals.

1. Introduction

Pyroelectric materials are of considerable current use in science and engineering. In doing so, the application fields of devices operating on the basis of these materials are progressively extended. Furthermore, the problems being solved with the use of pyroactive materials are growing in importance and topicality. The quality and variety of the properties of employed materials determine substantially the current status of optoelectronics. In recent years, the methods of producing new physical properties in the traditional piezoelectric crystals by means of generating thermodynamically nonequilibrium conditions in them have widely been developed [1, 2]. A symmetry change of the crystal lattice due to the action of an external field is a fundamental mechanism for the formation of new properties in crystals. The problem of fabricating materials possessing induced properties is being investigated for many years [3–5]. However, it is the standard practice to restrict the research of crystal properties to the conditions of a spatially homogeneous external action. This provides a possibility of ascertaining the symmetry properties of the induced polarization by the Curie principle immediately [6].

The harnessing spatially inhomogeneous actions (e.g., the inhomogeneous heating of a crystal) lead to radically new results. In that instance, there is an increase in the number of physical effects emerging in a crystal, and the mechanisms of their manifestation become more complicated. At the same time, a possibility to design entirely new pyroelectric devices is making its appearance. An important point is that the class of pyroactive materials can be largely expanded from 10 polar up to 20 piezoelectric classes. Moreover, the flexoelectric and thermopolarization effects take place along with the familiar secondary and tertiary pyroelectric effects [7, 8]. The first two effects are not in use as working effects for pyroelectric devices in spite of their appeal (they reveal themselves in all crystallographic classes).

The tertiary pyroelectric effect (TPE) is far in excess of the two indicated effects and differs fundamentally from the secondary pyroeffect by its symmetry (the last one takes place in the polar crystals only). TPE has become now a subject of close interest for designers of measuring apparatus owing to the following considerations. First of all, this effect manifests itself in all acentric crystals. In this connection, a range of problems that can be solved through its use is substantially extended. All pyroelectrics prove to be, in particular, of limited utility as sensitive elements for the sensors of intensive radiation fluxes due to their slight transparency in a middle IR spectral range. Second, the development of multifunctional devices measuring several characteristics of radiation fluxes in a real time simultaneously was realized due to the fact that the induced polarization possesses an intricate spatial distribution over the whole crystal volume [9]. New multifunctional sensors are now being created for the accomplishment of different functions simultaneously (e.g., the functions of output optical element and control-measuring device [10]).

2. Polarization at Radial Inhomogeneous Heating

It is known [6] that the tertiary pyroelectric effect consists in a polarization response to the inhomogeneous heating of a crystal and manifests itself as the piezoelectric effect induced by thermoelastic stresses appearing under such conditions. The secondary and tertiary pyroelectric effects are fundamentally distinct from each other by their symmetry despite the fact that they share a common piezoelectric nature. It is best to illustrate this distinction by the piezoelectric polarization calculation employing the thermodynamic potential on the supposition of a quasiequilibrium crystal state. The real contribution to a local polarization under this outline of analysis is represented by a sum of two contributions

$$\delta P_i(r,t) = d_{i\lambda} C_{\lambda\nu} \alpha_\nu \theta(r,t) + d_{i\lambda}\sigma_\lambda(r,t), \tag{1}$$

where $d_{i\lambda}$, α_ν, and σ_λ are the components of the piezoelectric moduli, the heat expansion tensor, and the tensor of thermoelastic stresses, respectively; $C_{\lambda\nu}$ are the elastic stiffness coefficients, and $\theta = T–T_0$ is the temperature increment, where T_0 and $T$are the initial and final temperatures of a some isolated local volume V_0. The first component in Eq. (1) is defined as a local secondary pyroeffect calculated assuming a free expansion of the volume V_0 to the value V_{free}. The second term presents a contribution to the polarization of thermoelastic stresses transforming the volume V_0 to its real value. This contribution is interpreted as TPE [11], and its symmetry is determined by a symmetry of the tensor σ_λ. The symmetry group of this tensor will be denoted as the external action group G_{act}. The crystal symmetry group in the field of such an action G is changed in accordance with the Curie principle

$$G \supseteq G_{\text{cry}} \cap G_{\text{act}}, \tag{2}$$

where G_{cry} is the symmetry group of an unperturbed crystal. Obviously, this principle establishes only a local symmetry under inhomogeneous heating. Generally speaking, the opportunity of its use for the TPE description as a whole remains an open question.

The calculation of characteristics of pyroelectric devices was faced with great difficulties. Really, if the approximations associated with a quasiequilibrium thermodynamic state in a crystal are unused, making an analytic determination of the polarization response requires a calculation of inner displacements of the crystal lattice. The reason is that the calculations founded on the determination of a macroscopic deformation [12] reveal only false contributions to the piezo- and flexoelectric effects. Numerical calculations should be carried out to get the closed relationships for output signals using the equations of state with consideration of all kinds of anisotropy (thermal, electric, and elastic ones). Such a procedure eliminates obtaining the general conclusions. All the aforesaid requires the development of new approaches to the description of induced polar states in a crystal caused by spatially inhomogeneous actions.

Here, we present an approximate method for the analysis of symmetry properties of the polarization induced in radially inhomogeneous temperature fields. The method based on the selection of several unipolar regions in a crystal volume with specific orientations of the polarization in them was first proposed in [13]. Such an analysis proves to be feasible in one-dimensional temperature fields and, in particular, under real conditions of measuring the characteristics of intense radiation fluxes. Methods of an approximate symmetry analysis will be given to study the properties of induced polar states in a crystal, being a round plate or a cylinder, under the axisymmetric heating by a sine-modulated radiation beam of radius r_0 with a wavelength in the crystal transparency band. The temperature increment distribution in a crystal θ (r, ω, t) can be represented as

$$\theta(r,\omega,t) = \theta_0 e^{i\omega t} \left\{ \begin{array}{ll} \frac{1}{qr_0} - I_0(qr)K_1(qr_0), & r \le r_0 \\ K_0(qr)I_1(qr_0), & r \ge r_0 \end{array} \right\}, \tag{3}$$

where θ_0 is a some constant, $q^2 = i\omega/a$, a is the thermal diffusivity, and $I_n(x)$ and $K_n(x)$ are the first- and second-kind Bessel functions of order n with a pure imaginary argument. It follows from analysis of expression (3) that the temperature field $\theta(r,\omega,t)$ is a continuous function at $r = r_0$, has only a weak dependence on r in the region $r < r_0$, and tends to zero as $e^{-(r-r_0)/\lambda}$ in the region $r > r_0$ (λ is the temperature wavelength in the crystal). Consequently, the crystal in the region $r > r_0$ remains cold under its irradiation.

It is believed approximately that the boundary between the specified regions is immovable in the context of a stationary character of the temperature field, while the symmetry groups in them are invariant. The analysis of a mechanical state of a heated region enables us to write the external action group in it as a limiting group

$$G_{\text{act}} \supseteq \infty/mmm, \quad r \le r_0, \tag{4}$$

where a rotation axis of the infinite order is perpendicular to the cut plane. Expression (4) is exact under the absolute clamping of a heated region in the cut plane (in the case of a plate) or over the entire lateral surface (in the case of a cylinder).

Certain difficulties arise in the derivation of the group $G_{\rm act}$ for a cold region ($r > r_0$), since this region is under an intense spatially inhomogeneous action (a loaded inside boundary of the region and a free outside surface should be kept in mind). The strong radial dependence of angular components of the thermoelastic stress tensor takes place at the boundary of the heated and cold regions. These components reverse sign for a distance of order of the temperature wavelength. Only the rotation axis n (if it is perpendicular to the cut plane) and the symmetry plane m (if it coincides with the cut plane) remain in the crystal symmetry group $G_{\rm cry}$ under these conditions. In order for this to happen, the external action group $G_{\rm act}$ must be a subgroup of the pseudovector symmetry group. If such symmetry elements are lacking in the group $G_{\rm cry}$, the piezoelectric polarization will be induced under dissymmetry conditions (except for the symmetry group D_n). The net results will look like

$$G_{\rm act} \supseteq \begin{cases} n/m, & n \text{ and } m \subset G_{\rm cry} \quad (a), \\ I, & n \text{ and } m \not\subset G_{\rm cry} \quad (b), \end{cases} \tag{5}$$

where I is the unit group. Relations (4) and (5) will suffice to determine a character of the polarization distribution in a crystal under axisymmetric heating. We note that expression (4) is true for a one-dimensional temperature field with thickness temperature gradient. In this case, group (4) exists in the whole volume of the crystal which is divided into three layers with the opposite direction of the polarizations in them.

3. Analysis of TPE Symmetry Properties in Acentric Crystals and Their Cuts

The symmetry properties of the polar states induced by radially inhomogeneous temperature fields are the same in a heated region as for a case of a temperature gradient directed inward a plate [13]. This is owing to the coincidence of the external action groups being described by the cylinder symmetry ∞/mmm in the both cases. For the cold region of the crystal in view of Eq. (5) and the Curie principle (2), we get the following results.

Monoclinic syngony. ***Class C_2.*** $G = I$ in the cuts containing the twofold axis. TPE manifests itself in these cuts under dissymmetry conditions.

Class C_s. $G = I$ in the cuts perpendicular to the directions $\bar{n}$ (n_1,0,n_3), and the polar state will occur under dissymmetry conditions.

Rhombic syngony. Class D_2. TPE exists in the cuts involving only one of the twofold symmetry axes under dissymmetry conditions.

Class C_{2v}. $G = m$ in the cuts normal to the directions $\bar{n}$ (n_1, n_2, 0) if only one of the components n_i is equal to zero. The transverse effect (the induced polarization vector perpendicular to the radiation flux lies in the plate plane) is found in these cuts. If none of these components become zero, TPE exists under dissymmetry conditions.

Tetragonal syngony. ***Classes C_4, S_4.*** Polar state existing under dissymmetry conditions takes place in both classes in the cuts perpendicular to the directions $\bar{n}$(n_1, n_2, 0).

Class D_4. TPE can manifest itself under dissymmetry conditions in those cuts, a normal to which lies in the plane passing through axis *4* and one of the twofold axes.

Classes C_{4v}, D_{2d}. The transverse effect takes place in the cuts coincident with one of the symmetry planes. The longitudinal effect (the polarization vector is directed along the incident radiation flux normally to the plate plane) exists in the D_{2d} class in the cuts perpendicular to the twofold axes.

Trigonal syngony. ***Class D_3.*** G= 2 in the cuts perpendicular to any one of the twofold axes, and the longitudinal TPE is found. TPE manifests itself in the cuts parallel to these axes under dissymmetry conditions.

Class C_{3v}. $G = m$ in the cut plane coincident with the symmetry plane, and the transverse effect can occur here. TPE is found in the planes perpendicular to the symmetry planes under dissymmetry conditions.

Hexagonal syngony. ***Class C_6.*** The polar state takes place under dissymmetry conditions in all cuts except for the cut perpendicular to axis *6*. The latter cut is characterized by the presence of the longitudinal effect.

Class C_{6v}. $G = m$ in all cuts containing axis *6*. The transverse TPE exists in these cuts. To obtain this result, the Hermann theorem should be taken into account.

Class D_6. This class manifests the same results as the class D_4.

Cubic syngony. ***Classes T, T_d.*** G= 3 (class T) and G=3m (class T_d) in cuts normal to the threefold axes. In these classes, respectively, the longitudinal and transverse effects take place. The longitudinal TPE exists in the cuts perpendicular to the twofold axes. TPE occurs in the cuts parallel to one of the twofold axes under dissymmetry conditions.

While studying the symmetry properties of induced polar states in a crystal, it has been found that an inhomogeneity of the temperature field and a kind of the crystallographic cut are of primary importance in forming the polarization spatial distribution. The symmetry properties of the polar states differ significantly from one another for the above-considered types of a one-dimensional temperature field. Really, in the case of a thickness temperature gradient, the polar state in each of the layers is characterized by the polarization vector coincident with the sole polar direction, which is induced by the inhomogeneous heating and is contained in the group G. The longitudinal TPE takes place only in the polar cuts, whereas the transverse one – in nonpolar cuts.

The induced polar states under the axisymmetric heating reveal a particular feature: the longitudinal and transverse polarization effects can manifest themselves in both polar and nonpolar cuts. In the general case, the polarization vector does not coincide with the sole polar direction which is contained in the group G. A number of results of a practical interest should be remarked. The longitudinal TPE occurring in classes D_2, D_4, and D_{2v} in the cuts normal to the twofold axes has the angular dependence related to the zero value of the total dipole moment of a mechanically free plate and the lack of the polarization in its heated region. The integral value of the tertiary polarization component in accordance with Eq. (1) is proportional to the mean value of thermoelastic stresses in the crystal volume. These stresses are induced by external forces acting on the body surface [14] and are equal to zero provided that a crystal surface is free from any external mechanical action. Moreover, if the threefold axis is contained in the group G in the cold region, the availability of the sole polar direction is not needed for the occurrence of a polar state. At the same time, the availability of the sole polar direction in the group G does not imply the existence only of the longitudinal effect along this direction.

A consequence of the research performed is that a series of new results outside of the context of the existing knowledge is found. This is concerned with the crystallographic cuts, for which the planes are perpendicular to the threefold axes. To take an example, the crystal symmetry groups $G = 3$ and $G = 3m$ for the crystallographic cuts [111] in a cubic syngony have been obtained in the case of an external field. It would seem that the polarization vector is to be directed along the sole polar axis that is contained in these groups. However, the transverse effect is available together with the longitudinal one, and the polarization vector does not coincide with the threefold axis direction. Furthermore, in analogous cuts of the crystallographic class D_3, where the longitudinal piezoelectric effect is strictly forbidden, the polarization vector is perpendicular to the sole polar direction. TPE is completely lacking in the indicated cuts of the crystals possessing the symmetry group D_6, where $G = 6$, in spite of the fact that the sole polar direction being available. This is due to the availability of rotations in the group C_6 which are not concerned with the threefold symmetry axis.

Let us deal with the Z-cuts for crystals with the symmetry groups C_{3h} and D_{3h}, for which the longitudinal effect is also forbidden. In the case under study, $G = \bar{6}$, and the sole polar direction does not belong to the group. Nevertheless, the transverse TPE exists in both cases. It is significant that the availability of the sole polar direction is not needed in the cut plane in all instances of the transverse TPE manifestation associated with the symmetry axis *3*. On the contrary, there is the angular dependence of the effect proportional to $\cos(3\varphi + \varphi_0)$. Thus, the invariance of the polarization spatial distribution under transformations of the group G holds in all the cases under discussion.

The experimental studies have been performed in cases which are of practical interest. The measurements have been made in a strong lattice absorption band of the crystal with the aim to increase the sensitivity of the method, whereas the axial symmetry was achieved by the modulation of a radiation flux at low frequencies, when λ in a crystal is greater than its thickness. The identical procedure was used to study the transverse TPE in different crystals having the symmetry axis C_3 in the cuts normal to this axis. The sensitive element was a disc of 22 mm in diameter and 0.2 mm in thickness. A system of 24 electrodes, which were insulated from one another and deposited on the lateral surface, enables us to determine the polarization angular distribution with an increment of 15°. For $LiNbO_3$ crystal, the transverse TPE occurs in the cold region only, the longitudinal one – in the whole volume. The longitudinal TPE is strictly forbidden in quartz in both regions, and only the transverse TPE takes place. A similar polarization distribution caused by the transverse TPE takes place in ZnSe crystals. The results are represented in Fig. 1. The polarization induced by the longitudinal TPE is oppositely directed in heated and cold regions (Fig. 2). The experimental results on the potential angle distribution correlate well with the theoretical ones.

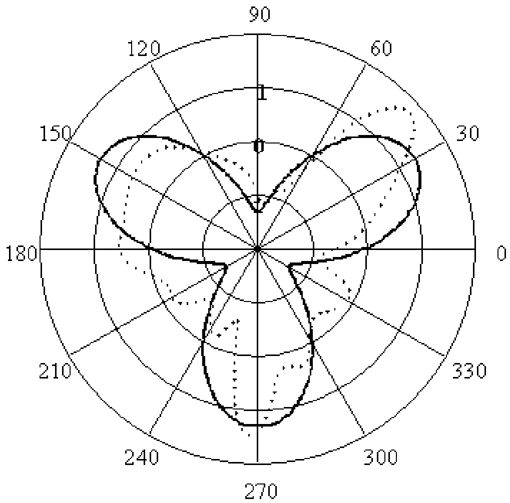

Fig. 1. Angular dependences of the electric potential for the transverse TPE. Solid line corresponds to theoretical calculations, the dashed line is experimental dependence

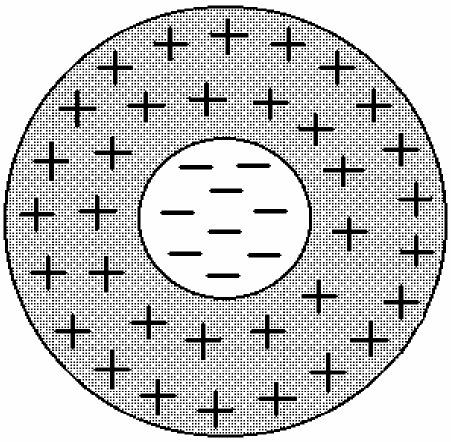

Fig. 2. Bound charge distribution induced by the longitudinal TPE

Other cuts of the indicated crystals, as well as other crystallographic classes, were examined. On the basis of these studies, the conception for the creation of pyroelectric devices with a high upper limit of the dynamical range and extended functional potentialities has been developed.

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СИМЕТРІЙНИЙ АНАЛІЗ ІНДУКОВАНОЇ ПІРОАКТИВНОСТІ У РАДІАЛЬНО НЕОДНОРІДНИХ ТЕМПЕРАТУРНИХ ПОЛЯХ

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Резюме

Вперше запропонована й розвинена концепція симетрійного підходу до вивчення індукованої термодинамічно нерівноважними умовами піроактивності у нецентросиметричних кристалах. Проведено симетрійний аналіз властивостей полярних станів і визначено всі можливі типи піроактивних кристалографічних зрізів у кожному із двадцяти п'єзоелектричних класів за умов радіально неоднорідних температурних полів. Встановлено, що третинний піроелектричний ефект може проявлятися як у полярних, так й у неполярних кристалографічних зрізах, а вектор поляризації може не збігатися з особливим полярним напрямком, що міститься в групі, яка описує симетрію кристала в полі зовнішнього впливу. Результати симетрійного аналізу узгоджуються з експериментальними даними, які вперше отримали пояснення на його основі. Розвинутий симетрійний підхід виявився ефективним методом визначення основних особливостей просторового розподілу поляризації, інформація про які є необхідною при розробці фізичних принципів побудови нового класу сенсорних пристроїв, що діють на основі індукованої піроактивності у нецентросиметричних кристалах.