

Thermoelastic polarization and other effects in polar semiconductors

S.O. Voronov*, V.A. Kazmirenko, Yu.M. Poplavko

National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute",
37 Beresteiskyi Avenue, 03056 Kyiv, Ukraine

*Corresponding author e-mail: s.voronov.aph@gmail.com

Abstract. Electrical polarization and associated effects are now gaining importance for electronics due to growing application of wide-bandgap polar semiconductors such as gallium arsenide and gallium nitride. The internal polarity of the structure of such semiconductors has significant impact on millimeter wave losses as well as on the technological features and application of electronic devices based on polar semiconductors. It has been shown that any piezoelectric has an intra-crystalline polar moment, even if the piezoelectric crystal does not belong to the pyroelectric symmetry. A new effect of thermoelastic polarization in polar-neutral crystals is described and a number of possibilities for its implementation are discussed. The experimental study of the internal polarity in piezoelectrics is provided by the partial limitation of thermal strain method. It is believed that thermoelastic polarization must be taken into account in the technology of polar semiconductors as enabling creation of integrated sensors based on them.

Keywords: polar semiconductors, piezoelectricity, pyroelectricity, integrated sensors.

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1. Introduction

Polar crystals include 20 classes of non-centrosymmetric crystals with important for applications in electronics properties such as piezoelectric and pyroelectric effects. The relevance of this article is given by the fact that among various polar crystals, there are wide-bandgap $A^{III}B^V$ and $A^{II}B^V$ semiconductors, the use of which is rapidly increasing, especially for devices operating in the microwave range. An example of a promising semiconductor is gallium nitride, which has a polar wurtzite structure. Other representatives of polar crystals, namely the crystals of the gallium arsenide type, have a sphalerite structure. Their natural intrinsic polarity significantly increases absorption of microwave radiation especially in the millimeter wavelength range, which should be taken into account for applications of such semiconductors. Moreover, polar properties may be considered in the technology of respective devices. For example, epitaxial films of GaN, AlN and InGaN crystals usually grow just along their polar axes. Although the polarity of these nitrides has been studied by various methods, the obtained results are often controversial [1].

In this work, a technique for measuring hidden polarity of piezoelectric crystals by determining their "pyroelectric" response under conditions of limited thermal deformation has been developed. Although the effect of partially limited thermal deformations on the

electrical properties of polar crystals was studied on bulk samples, the obtained results are also important for widely used technologies of thin-film functional devices, since the influence of thermal and elastic properties of a used substrate is especially significant for them [2].

As will be also shown in this paper, the intrinsic polarity can open up new applications of wide-bandgap semiconductors in the field of matrix sensors for creating integrated devices, where a sensor element is combined with amplifiers and a read-out circuit on a single chip. In this case, the piezoelectric or pyroelectric properties of a polar crystal are utilized to transform thermal or mechanical impacts in the electric response. In principle, thermal sensors can be developed based on the new thermoelastic polarization effect described below (similarly to existing sensors, based on detecting dynamic changes in the pressure of a liquid, the well-known volumetric piezoelectric effect). It is important to note that these effects manifest themselves in any piezoelectric (even with a non-pyroelectric symmetry), but under conditions of limited thermal or piezo-deformation, which can be realized using appropriate designs.

The following description mainly concerns a new effect of thermoelastic polarization (TEP). A design that enables limiting some crystal deformations is proposed as well as the expressions for calculating the intensity of the mentioned effect at different crystal orientations are obtained. Externally, thermoelastic polarization is

observed and can be applied as a regular pyroelectric effect. However, the physical mechanism of TEP differs from those of the primary, secondary and tertiary pyroelectric effects. Hence, arrangement of TEP-based sensors differs from the designs of pyroelectric sensors. This difference is due to the fact that usual pyroelectric effect arises only in 10 pyroelectric classes of crystals and has the maximum along a peculiar polar axis. In the case considered here, pyroelectricity can be seen both in free and in clamped crystals. In the latter case, only primary effect is possible, while secondary pyroelectric effect usually predominates in mechanically free crystals and at low temperatures, when the intensity of thermal motion is not sufficient to cause the primary effect.

A peculiarity of thermoelastic polarization is that it is possible in all the 20 classes of polar structures, and, moreover, precisely along one of the polar-neutral axes of a crystal (including 10 classes of non-pyroelectrics, *i.e.*, “exclusively piezoelectrics”). In this case, TEP manifests itself only under artificially created conditions, when thermal deformation is allowed along a polar-neutral crystal axis, *i.e.*, in *partially clamped* and, therefore, stressed crystals. It is remarkable to note that TEP can be also observed in 10 classes of pyroelectrics. We studied this effect in lithium niobate crystals. It turns out that polar sensitivity along the polar-neutral axes is close in magnitude to the pyroelectric response along a peculiar polar axis. Indeed, a thin plate of a LiNbO_3 crystal, cut perpendicularly to one of the $[111]$ axes and stuck onto a silica glass substrate (thermal expansion $\alpha \approx 0$ that prevents only planar thermal deformations) makes it possible to obtain TEP with the artificial pyroelectric coefficient $\gamma_{\text{TEP}} = \gamma_2 = 40 \mu\text{C}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ that is only slightly lower than the usual pyroelectric coefficient of LiNbO_3 $\gamma_3 = 50 \mu\text{C}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ [3]. This allows one to assume that influence of internal polarity in wide-bandgap polar semiconductors with a wurtzite structure (such as gallium nitride) may be significant not only in the pyroelectric axis direction.

2. Difference between polar and polar-neutral crystals

The most important structural elements of all the polar crystals of the 20 classes are their polar axes, along any of which maxima of the piezoelectric effect are observed. At that, in the 10 *pyroelectric* classes of polar crystals one of the polar axes is “peculiar”, since not only the piezoelectric, but also the pyroelectric effect manifests itself along it to the greatest extent. The remaining polar axes are polar-neutral ones. Although they are piezo-active, no pyroelectric effect is possible along them both in mechanically free and clamped crystals.

The difference between the polar-neutral axes and a peculiar polar axis is shown in Fig. 1. Four polar axes in a piezoelectric sphalerite (Figs 1a and 1b) correspond to the maxima of the piezoelectric effect that is manifested when a directional mechanical force (having a vector symmetry) acts on such crystal. However, no electric response from a polar-neutral crystal is possible in a case of a scalar action on it (such as uniform heating or hydrostatic pressure), since the location of polar-neutral axes provides full compensation of the crystal internal polarity. It is appropriate to note that a scalar impact causes both thermoelectric and mechanoelectric responses along the pyroelectric “peculiar” polar axis. Nevertheless, presence of polar-neutral axes follows from many others experiments. For instance, their existence is confirmed by the fact that growth of crystals from liquid phase occurs just along these axes. Furthermore, the surfaces of plates, cut perpendicularly to the polar-neutral axes, have different rates of etching and show quite different chemical characteristics.

For a simplified comparison of two polar cubic structures, one of the four polar axes of sphalerite will be enlarged such as in Fig. 1c. As a result, the pyroelectric structure of wurtzite appears, which can generate both pyroelectric effect and volumetric piezoelectric effect even under scalar influence. It will be shown below how uncompensated polarity similar to that in Fig. 1c can be

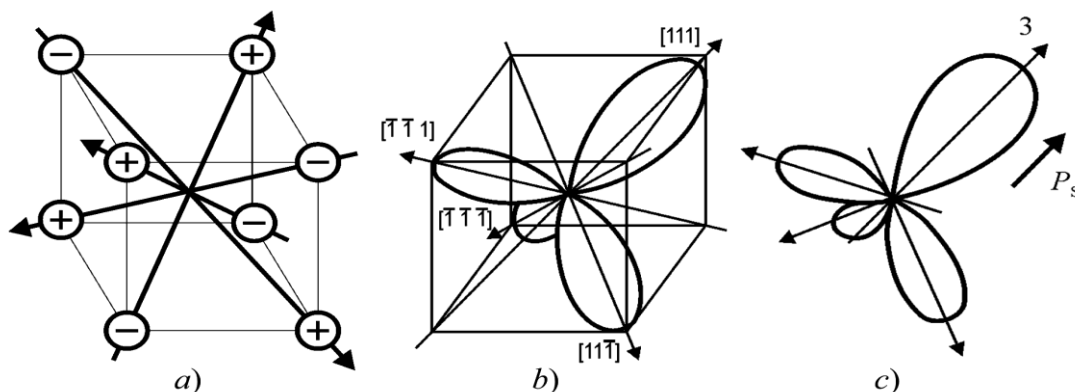


Fig. 1. Intrinsic polarity in crystals: *a* – four polar-neutral axes in a cubic crystal; *b* – spatial distribution of piezoelectric responsivity in a polar-neutral crystal (only positive directions of the (111) axes are shown); *c* – appearance of an additional dipole component, which means the pyroelectric polarization; this model may be also applied to explain the coexistence of polar-neutral sphalerite structure (*b*) with polar wurtzite structure (*c*) in zinc blende or in GaN type crystals. Here, P_s is the spontaneous polarization along a third-order polar axis.

obtained in a crystal with a fully compensated internal polarity (see an example in Fig. 1b by creating certain boundary conditions).

It is expedient to compare the effect of thermoelastic polarization with other long-studied thermoactivated polarization effects. At a first glance, TEP may seem to be classified as a “secondary” pyroelectric effect due to the similarity of their mechanisms and calculation methods. However, such a definition is incorrect, since secondary pyroelectric effects occur in mechanically free crystals, while TEP is observed only in partially clamped crystals. Moreover, TEP should be compared to a tertiary pyroelectric effect [3], since both of them arise due to thermal stresses in piezoelectrics. However, in a case of a tertiary pyroelectric effect, the pyroelectric-like response is due to the temperature inhomogeneity of a crystal (which is affected by the vector $\text{grad } T$). At the same time, TEP looks like a regular pyroelectric effect, which occurs when a crystal is *uniformly* heated or cooled. It is important to note that TEP arises when certain strains in a crystal are limited, *i.e.*, it is a consequence of the peculiar boundary conditions. This effect, induced in piezoelectrics by heterogeneous elastic stress, may be considered as the result of a superposition of the crystal symmetry and the symmetry of the boundary conditions. One possible definition of TEP might sound like “the pyroelectricity in partially clamped piezoelectrics”. However, using here the term “thermoelastic polarization effect” more adequately points to the physical mechanism of this phenomenon.

It is demonstrated below that thermoelastically induced polar response can be applied to measure compensated polarity components in all the 10 classes of “veritable” piezoelectrics.

3. Description of peculiarities of polar crystals

At a first glance, it might seem strange to obtain pyroelectric type thermoelastic polarization in piezoelectric crystals. But, actually, there are many experimental evidences of similar manifestation of electric, mechanical and thermal properties in different types of polar crystals. Below some examples of observations of peculiar

“hidden” polarity in piezoelectrics, which are considered polar-neutral crystals, are presented.

It should be noted first that during crystallization, polar crystals decrease in density as compared to their melt. For example, a growing GaAs polar crystal floats in its melt as ice in water [2]. It may be concluded therefore that fixation of polar bonds expands the material, simultaneously transforming its structure into a non-centrosymmetric one. Secondly, chemical properties of polar crystals exhibit unipolarity on the crystal surface. For instance, it has long been known [4] that etching of a quartz crystal occurs more rapidly at the “positive” end of a polar X -axis, while the etching is slower at the “negative” end of this axis. Hence, the etched patterns for quartz plates are very different for the “+” and “-” surfaces. In the same way, one can see considerable difference in the chemical properties of two surfaces of a *polar* [111]-plate in cubic polar GaAs crystals [3]. It is worth mentioning that just chemical unipolarity of polar crystals is used in studies of ferroelectric domains [5].

It is remarkable that polar crystals show unique thermal properties. Their thermal conductivity is significantly lower than that of non-polar crystals (for example, the thermal conductivity of GaAs is ~ 5 times less as compared to Si) due to the peculiarities of the phonon dissipation process in polar structures [6]. In such crystals, the phonon group velocity reduces because the acoustic phonon branch bends down at approaching the Brillouin zone boundary (Fig. 1a). This leads to a strong increase of the acousto-optic interaction and slowing down the speed of short-wave thermal phonons. On the contrary, centrosymmetric crystals, such as Si, have no anomalies in the acoustic or optical phonon dispersion. Another curious feature of the thermal properties of polar crystals is that the thermal expansion coefficients of the latter, unlike showing the classic dependence $\alpha(T) \sim T^3$, acquire negative values [7]. This mysterious property is explained by a change in the nature of inter-atomic attraction of neighboring ions. For the same reason, namely due to negative thermal expansion, the pyroelectric coefficient of some polar crystals changes its sign at low temperatures [8].

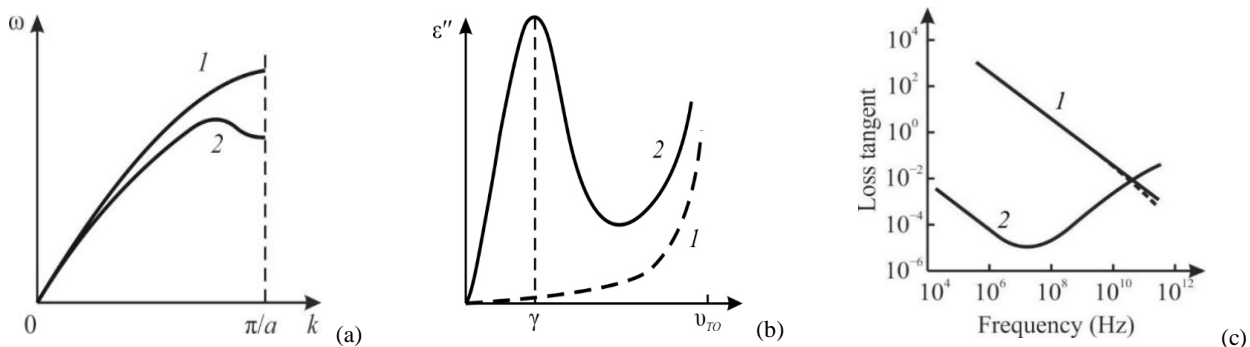


Fig. 2. Comparison of thermal and dynamic properties of polar and non-polar crystals: *a* – acoustic branch in the Brillouin zone for non-polar (1) and polar (2) crystals, *b* – frequency dependences of the absorption coefficient $\epsilon'' = \epsilon' \tan\delta$ for non-polar (1) and polar (2) crystals, and *c* – microwave losses in non-polar Si (1) and polar GaAs (2) crystals.

It should be further noted that in polar crystals, the so-called fundamental high frequency absorption ($\epsilon'' = \epsilon' \tan \delta$) in the microwave range substantially exceeds the respective absorption by centrosymmetric crystals [9]. This feature of polar crystals correlates with their acoustic phonon spectrum near the Brillouin zone boundary (Fig. 2a) strengthening the interaction between optical and acoustic phonons. As known [5], in any ionic crystal, a “tail” from the fundamental absorption maximum is visible in the microwave range (curve 1 in Fig. 2b) due to dielectric dispersion of ionic polarization (visible in the far-infrared (IR) range of waves). Hence, microwave losses occur at a level of $\tan \delta \approx 10^{-4}$. However, additional quasi-Debye lattice losses with the maximum located in the very-far IF region (curve 2 in Fig. 2b) are observed in polar crystals. This feature is characteristic not only of $A^{III}B^V$ and $A^{II}B^{VI}$ semiconductors, but also observed in many others polar crystals [9]. Among them, there are ZnO, AlN, BN, etc. polycrystals, the microwave losses in which are unexpectedly big ($\tan \delta \approx 10^{-2}$) and cannot be explained by usual loss mechanisms. These materials have low conductivity (hence, it cannot affect the microwave losses), and their frequency of lattice resonance ν_{TO} is too large to create a noticeable effect on the microwave losses.

Fig. 2c shows our experimental evidence of an increased microwave absorption in a polar crystal as well as opposite character of the frequency dependences of absorption in non-polar and polar crystals, which deserves peculiar consideration.

Comparison of the microwave absorption in polar silicon and polar gallium arsenide is shown in Fig. 3 (the methodology of these measurements is described in [9]). Silicon has purely electronic nature of polarization, hence, its permittivity at microwave frequencies is not frequency-dependent. Therefore, no microwave dielectric absorption is possible. Hence, the losses in silicon are determined only by the electric conductivity σ and may be described as $\tan \delta = \sigma / (\epsilon_0 \epsilon' \omega)$. The experimental results shown in Fig. 3a confirm such dependence. The nature of the latter is not affected by the conductivity increase with temperature. In Fig. 2c, one can notice a greater decrease in losses with frequency than the one expected according to the given formula. This decrease is due to the decrease in the electron mobility at submillimeter wave frequencies. Therefore, in silicon as well as in others covalent semiconductors, only the conductivity defines absorption of microwave energy. It is also clearly seen that the increased microwave losses in gallium arsenide are not due to its conductivity.

The experimental data obtained for a GaAs crystal are presented in Fig. 3b. These data show that polar structure of semiconductors indeed produces a significant effect on the microwave absorption. One would expect that the microwave absorption properties of such semiconductors are mainly due to the fast electronic and ion polarization processes, which make virtually no contribution to absorption in the microwave range and ensure frequency independence of the dielectric constant (Fig. 3b).

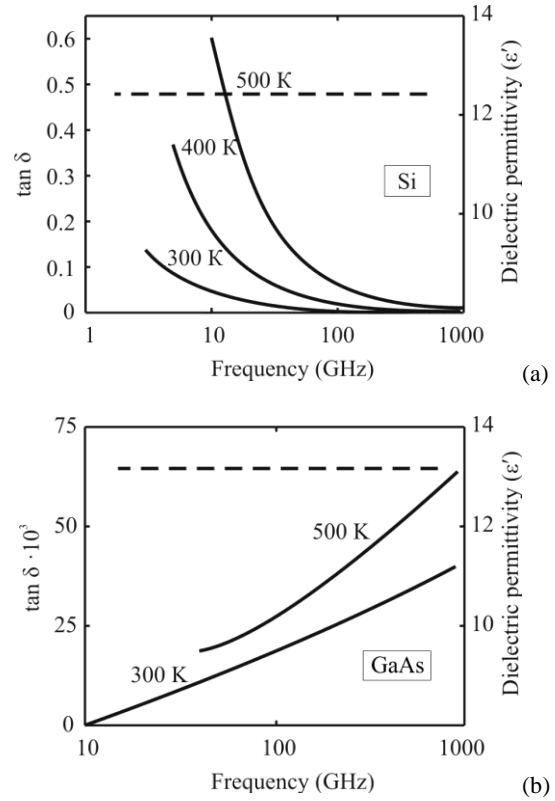


Fig. 3. Frequency dependences of microwave losses $\tan \delta$ (solid lines) and permittivity ϵ (dotted lines) in the gigahertz range for: a – high-resistance silicon and b – gallium arsenide.

However, along with this, there is also a quasi-Debye mechanism of energy absorption of millimeter and especially submillimeter waves. Due to the significant electromechanical coupling in polar crystals, a specific relaxation process occurs, caused by the interaction of acoustic and optical phonons. This leads to a “leakage” of the energy of optical phonons excited by an electric field, into a “thermal reservoir” of acoustic phonons. This effect is enhanced at shorter wavelengths, so that the loss coefficient of a polar crystal increases with increasing frequency.

In wide-bandgap polar semiconductors, below the frequency of about 100 GHz, the dielectric losses due to the quasi-Debye relaxation are not large enough to prevent use of such semiconductors as high-quality substrates and for active devices. Moreover, due to the big bandgap values, the thermal stability of these materials is significantly greater as compared to that of silicon. Nevertheless, quasi-Debye microwave absorption becomes noticeable in terahertz applications, so that non-polar silicon may have an advantage.

It should be noted in conclusion to this section that interdependence of internal polarity and crystal conductivity might be a significant physical phenomenon. For example, intrinsic electric polarity should not be neglected even in classifying semiconductors. Non-polar crystals (such as Si or Ge) are characterized by indirect band gaps, while polar semiconductors such as $A^{III}B^V$

(with mainly piezoelectric symmetry) and A^{II}B^{VI} (with pyroelectric symmetry) crystals are direct band gap ones. At that, distinction between pyroelectrics and piezoelectrics is not so fundamental and consists in the different spatial distributions of their polar bonds.

4. Implementations of thermoelastic polarization

The thermoelastic polarization concept refers to a possibility to get a pyroelectric like effect in a polar-neutral cut of a piezoelectric by its homogeneous heating. This becomes possible if a part of the thermal strain is artificially restricted. As known, the pyroelectric effect is defined as an electric response of a polar crystal to a *uniform* alteration in the crystal temperature. The pyroelectric effect is conventionally divided into the primary and the secondary components characterized by the coefficients $\gamma^{(1)}$ and $\gamma^{(2)}$, $\gamma_i^{X,E} = \gamma_i^{(1)} + \gamma_i^{(2)}$. Here, $i = 1, 2, \text{ and } 3$ because γ_i is a vector. The symbol X means the stress E is the electric field, and the superscripts indicate constancy of these parameters. In fact, the values of both electric field and mechanical stress should not be zero, but it is assumed that they remain unchanged during determining the pyroelectric coefficient.

Contribution of the primary pyroelectric effect can be experimentally found, when a mechanically clamped crystal is studied (*i.e.*, thermal strain is absent: $x_n = 0$ and $\gamma_i^{(1)} = \gamma_i^{(x)}$). The secondary effect is caused by piezoelectric transformation of the thermal strain: $\gamma_i^{(2)} = d_{im}^T \cdot c_{mm}^{X,E} \cdot \alpha_n^{X,E}$, where the tensor subscripts $m, n = 1, 2, \dots, 6$, d_{im}^T is the piezoelectric module, $c_{mm}^{X,E}$ is the elastic stiffness, and $\alpha_n^{X,E}$ is the thermal expansion coefficient, respectively. In what follows, the technique for calculating the secondary effect will be used in the description of the new thermoelastic effect: $d_{3'1'} = d_{3'2'} = -d/2\sqrt{3}$.

The pyroelectric coefficient $\gamma_i^{X,E}$ is usually determined from electric current measurements on a mechanically free crystal (the stress $X_m = 0$) and under electrically free conditions (the crystal is placed in a closed circuit, $E_i = 0$). The contribution of the secondary effect is the difference between the pyroelectric coefficients of the free and the clamped crystal, $\gamma_i^{(2)} = \gamma_i^{X,E} - \gamma_i^x$. It is important to note that symmetry requirements permit both primary and secondary pyroelectric effects only in 10 pyroelectrics of the 20 classes of polar crystals. In the remaining 10 piezoelectric (not pyroelectric) classes, any scalar (homogeneous) influence, including temperature change, cannot result in a vector (electric) response under homogeneous boundary conditions, *i.e.* if the crystal is completely free mechanically ($X_m = 0$) or it is entirely clamped ($x_n = 0$).

Here, a case of *anisotropic* mechanical conditions on the crystal is discussed, which makes it possible to obtain thermoelastic polarization, for which the concepts

of primary and secondary effects lose their meaning. To excite the desired electric response in a piezoelectric by homogeneous thermal influence, inhomogeneous boundary conditions are required. In other words, new mechanical conditions will be added (applicable to all the 20 polar classes of crystals). Creation of the mentioned boundary conditions for a polar crystal opens up a possibility of realizing only one component of thermal strain, while its other components are not allowed. That is, a case of a partially clamped crystal will be considered.

An experimental and theoretical study of thermoelastic polarization using a well-studied polar GaAs crystal with the $43m$ cubic symmetry as an example is provided below. Since the thermal expansion coefficient of a cubic crystal is isotropic, spatial distribution of the thermoelastic electric response is defined by the piezoelectric module. Its value has maxima along the 4 polar-neutral axes of the 3rd order, as shown in Fig. 1a. At this, the piezoelectric effect along the main axes of Cartesian coordinates x, y, z is absent. The spatial distribution of the piezoelectric modulus, which is a rank 3 tensor, is shown in Fig. 4a. The indicatory surface looks like eight identical surfaces joined in the centre of a cube. It is evident from Fig. 4a that the response coefficient γ_{TEP} can be found as the components of the radius-vector directed from the centre of the cube to its intersection with an indicatory surface.

The studied GaAs sample was a thin plate with deposited electrodes, soldered on a thick rigid substrate made of fused silica, which has practically zero thermal expansion coefficient, $\alpha_{sub} = 0$. The normal to the GaAs plate was oriented along one of the polar-neutral directions of the piezoelectric crystal, which, due to limitations of planar strain, became a peculiar polar axis (in accordance with the Curie's superposition principle). Any tangential deformation of a sample was completely suppressed during heating or cooling by a Peltier element. Only a strain in the direction of the polar-neutral axis [111] perpendicular to the sample surface was permitted. No shear deformations could be created by a *uniform* heat flux, while rather big area of a plate in this experiment allowed one to neglect the boundary effects. The resulting pyroelectric current was measured with a galvanometer, and these data served as the basis for calculating the "pyroelectric" coefficient using a standard method.

It follows from Fig. 4b that an electrical response in a crystalline plate is possible due to the *longitudinal* piezoelectric effect. However, even in an oriented but mechanically free crystal, it should be absent being completely compensated by the transverse piezoelectric effect. Therefore, all the components of the piezoelectric module must be examined as the next step. It is well known that in the main installation of a $43m$ symmetry crystal using Cartesian axes, the piezoelectric module of a sphalerite crystal is described by the matrix shown in Fig. 5a. However, this matrix represents only the components of the shear effect, which are equal, $d_{14} = d_{25} = d_{36}$, and may be denoted simply as d therefore.

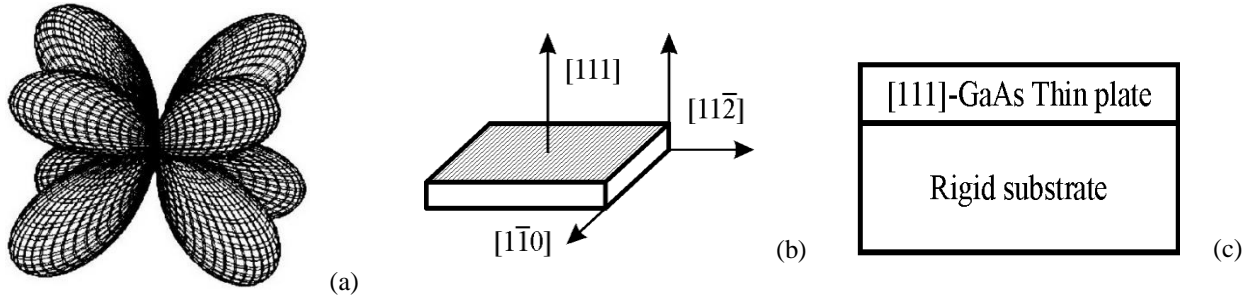


Fig. 4. *a* – spatial distribution of the electrical response intensity in a sphalerite crystal; *b* – orientation of studied GaAs plate; *c* – a plate soldered to a fused silica substrate, the hatching shows the top electrode.

It follows from Fig. 5a that in the basic setup of a cubic crystal (based on Cartesian axes), for crystal plates with the (100), (010) and (001) orientations, both longitudinal (d_{11} , d_{22} , d_{33}) and transverse components (d_{12} , d_{13} , d_{21} , d_{23} , d_{31} , d_{32}) of the piezoelectric module are equal to zero. It means that electric response is impossible in the plates cut parallel to the cubic faces of a $\bar{4}3m$ symmetry crystal, if the external influence on the crystal is scalar in nature. The shear components of the piezoelectric module are also inactive in such case. It is quite possible that this is a reason why polar effects in gallium arsenide are usually not taken into account in most experiments and in electronic device technology, in view that just the plates with the mentioned orientations are typically used.

To observe the thermoelectric effect in a $\bar{4}3m$ symmetry crystal, the latter must be installed so that one of the new $3'$ -axes coincides with the polar-neutral axis [111]. In this case, the new axis $1'$ should be directed perpendicular to the (111) plane, while the new axis $2'$ is specified by the Cartesian coordinates, as can be seen in Fig. 4b. All components of the resulting new matrix are expressed in terms of the shear modulus d taken from the basic crystal setup (Fig. 5a). The thermoelastic polar

$$d_{im} = \begin{bmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36} \end{bmatrix},$$

a

$$d'_{i'm'} = \begin{bmatrix} 0 & 0 & 0 & 0 & -\frac{d}{\sqrt{3}} & \frac{2d}{\sqrt{6}} \\ \frac{d}{\sqrt{6}} & -\frac{d}{\sqrt{6}} & 0 & -\frac{d}{\sqrt{3}} & 0 & 0 \\ -\frac{d}{2\sqrt{3}} & -\frac{d}{2\sqrt{3}} & \frac{d}{\sqrt{3}} & 0 & 0 & 0 \end{bmatrix}$$

b

Fig. 5. Comparison of the piezoelectric module matrices for gallium arsenide: *a* – the main installation for a crystal of the $\bar{4}3m$ symmetry and *b* – installation, which allows the study of thermoelastic polarization.

effect is described by the third row of the matrix shown in Fig. 5b. It characterizes the piezoelectric properties of a discussed crystalline plate, which has a longitudinal piezoelectric module $d_{3'3'} = d/\sqrt{3}$ and two components of the transverse effect, $d_{3'1'} = d_{3'2'} = -d/2\sqrt{3}$. These components are maximum in the crystal sections oriented perpendicular to the third-order axis (which is the spatial diagonal of a cube). The highest polar sensitivity in $A^{III}B^V$ crystals coincides with those directions, in which the electronic density along an A–B ionic bond is maximum in the vicinity of the B ion. Note, that the third row of the matrix in Fig. 5b does not contain piezoelectric shear components. The details of the calculations are presented as an exercise for students in the textbook [9].

Next, we consider only the third row of the transformed matrix shown in Fig. 5b, since only this row defines the studied effect under the conditions shown in Figs. 4b and 4c. It can be seen that the part of the piezoelectric response induced by the longitudinal strain x_3 and characterized by the piezoelectric modulus $d_{3'3'}$ is equal to other two parts induced by the transverse strain x_1 and x_2 and described by the components $d_{3'1'}$ and $d_{3'2'}$ having an opposite sign. In a stress-free cubic crystal, all the strain components are equal, $x_1 = x_2 = x_3$. It can be seen from Fig. 5b that the sum of the transverse and longitudinal piezoelectric coefficients for a non-pyroelectric crystal is zero, because the piezoelectric effect created by the longitudinal strain component x_3 is compensated by the action of two transverse strain components x_1 and x_2 . Therefore, any electrical response with a uniform effect on the crystal is impossible, and a stress-free polar (111)-plate of a GaAs type crystal is not sensitive to homogeneous excitations.

However, limiting some of the mentioned strain components (x_3 or $x_1 + x_2$) can turn a (111)-plate of a GaAs crystal into an artificially created “pyroelectric”. In practice, it is easier to limit the planar deformation using a simple mechanical design. In this case, only a strain x_3 can be induced along the plate thickness precisely in the direction of the polar-neutral axis [111], which is transformed into a “peculiar” polar axis. This effect is impossible both in a free crystal and in a clamped one since thermoelastic polarization appears only as a result

of non-isotropic partial clamping. Only partially clamped piezoelectric crystals exhibit thermoelastic polarization as well as the volumetric piezoelectric effect.

Calculations of the thermoelastic polarization coefficient $\gamma_{TEP} = dP_i/dT$ uses the allowed strain x_3 , while the mechanical stress component X_3 is zero. Another boundary condition is $E_3 = 0$, *i.e.*, the crystal is assumed electrically free (closed circuit). As shown in [9], it is necessary to take into account that in cubic crystals $s_{11}^{E,T} = s_{22}^{E,T}$ and $X_1 = X_2$. In the peculiar installation of the crystal shown in Fig. 5b, the parameter $\gamma_3 = dP_3/dT = 2d_{31} \alpha / (s_{11}^{E,T} + s_{12}^{E,T})$. After conversion of the parameters of this expression into the standard installation of the crystal used in reference books, we obtain

$$\gamma_{111} = \frac{2\sqrt{3} d_{14} \alpha}{4s_{11}^{E,T} + 8s_{12}^{E,T} + s_{44}^{E,T}}.$$

The gallium arsenide parameters required for TEP calculation are the thermal expansion coefficient $\alpha = 2.8 \cdot 10^{-6} \text{ K}^{-1}$, elastic compliance components $s_{11}^{E,T} = 12 \cdot 10^{-11} \text{ m}^2/\text{N}$, $s_{12}^{E,T} = -4.6 \cdot 10^{-11} \text{ m}^2/\text{N}$, $s_{12}^{E,T} = -4.6 \cdot 10^{-11} \text{ m}^2/\text{N}$ and $s_{44}^{E,T} = 17 \cdot 10^{-11} \text{ m}^2/\text{N}$, and piezoelectric module $d = 2.7 \cdot 10^{-12} \text{ C/N}$. The calculation shows that $\gamma_{111} = \gamma_{TEP} = 1.5 \mu\text{C} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$ for GaAs. This means that the figures of merit of a possible sensor would be the following: the current sensitivity $S_J = \gamma/C_V = \sim 0.2 \text{ A} \cdot \text{m} \cdot \text{W}$ and the voltage sensitivity $S_V = \gamma/(C_V \epsilon_0 \epsilon) = \sim 0.02 \text{ B} \cdot \text{m}^2/\text{J}$, where C_V is the thermal capacity. At this, the recommended frequency of heat flux modulation is 1 kHz, while the penetration depth of the heat flow into GaAs is $\delta = (a/(\pi\nu))^{1/2} \sim 100 \mu\text{m}$. Here, $a = 4 \cdot 10^{-5} \text{ m}^2 \cdot \text{s}$ is the thermal diffusivity. In this layer, a temperature wave with the amplitude ΔT would generate an electric voltage $U = E\delta = \gamma\Delta T\delta/(\epsilon_0\epsilon)$, *i.e.*, $U \sim 2 \text{ V}$ at $\Delta T = 1 \text{ K}$.

Preliminary estimations show that the TEP coefficient of GaN is much higher than that of GaAs. Therefore, GaN has better all the other thermoelectric characteristics. It should be also noted that the respective TEP coefficient for quartz crystal is $\gamma_{TEP} = \gamma_{100} = 2.6 \mu\text{C} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$, and it is also observed along the three polar-neutral axes. These effects are not weak. For example, the pyroelectric coefficient of well-known tourmaline is $4 \mu\text{C} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$. In bismuth germanate $\text{Bi}_{12}\text{GeO}_{20}$ belonging to a cubic symmetry of the class 23, the polar direction is [111], and the maximum TEP coefficient $\gamma_{111} = 20 \mu\text{C} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$. At this, the mentioned crystals are dielectrics.

The obtained results may find a number of applications.

Firstly, an additional method of quantifying polarity of semiconductors of a sphalerite structure (GaAs, GaAl, GaN, AlN and their solid solutions) is proposed. This method may be also used to study crystals with a wurtzite structure. That is, it is possible to estimate spatial distribution of intrinsic polarity, which may play a role for development of devices.

Secondly, although the studies were carried out on bulk materials, the described method of calculations and measurements is also applicable to thin films. The properties of the latter can be controlled in wider limits as compared to bulk materials by creating stresses and strains due to specific boundary conditions. This scientific direction, an “elastic strain engineering”, has become established [2]. In the framework of this direction, it is possible to change the local crystalline symmetry and obtain completely new properties of films.

Thirdly, some devices containing polar semiconductor plates installed in wrong orientations can generate polarization noises into the microcircuits where they are used. These noises can be induced in the semiconductor plates by external vibrations or thermal fluctuations. Our study shows that this circumstance must be taken into account.

Fourthly, polar-neutral piezoelectric crystals may be used as far infrared sensors or volume-piezoelectric effect sensors integrated with amplifiers in a single crystal. For example, in a possible sandwich composition, the top layer may be a “pyroelectric” transducer integrated with an amplifier and readout circuit located in the bottom layer. Note that all of the mentioned crystals are simultaneously thermoelectric and piezoelectric converters and have very high electron mobilities, which is necessary to amplify the sensor signal.

4. Conclusions

A wide range of physical properties of various types of polar crystals is analyzed. Based on the analysis results, the similarity of the physical mechanisms of internal polarity is proven. The mentioned polarity inevitably leads to an increase in microwave losses, which may be significant for wide-bandgap semiconductors such as gallium arsenide. A new effect of thermoelectric polarization in polar-neutral piezoelectric crystals (analogous to the secondary pyroelectric effect) is investigated. This effect appears when peculiar boundary conditions, under which the crystal can be deformed only in one of its polar-neutral directions, are created. This partial thermal deformation method is used to study compensated (hidden) polarity. The scientific novelty of this work is that it has found the boundary conditions, under which one of the polar-neutral axes of a crystal is artificially transformed into the “peculiar” polar axis, providing thermoelastic polarization similarly to the pyroelectric effect. The novelty of this work for electronics may be predicting appropriate orientations of the device active elements that must be chosen to avoid vibration noise and influence of temperature fluctuations. Moreover, use of the thermoelastic effect opens up the possibility of creating single-chip temperature sensors with co-integrated “pyroelectric” layers and amplifiers.

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Authors' contributions

Voronov S.O.: formal analysis, investigation, data curation (partially), visualization, writing – original draft, writing – review & editing.

Authors and CV



Voronov S.O. Professor, Doctor of Technical Sciences, Professor of the Department of Applied Physics of the “Igor Sikorsky Kyiv Polytechnic Institute”. Author of more than 300 scientific publications. His main research interests are materials and technologies based on new physical principles. E-mail: s.voronov@kpi.ua, <https://orcid.org/0000-0002-0053-0381>



Kazmirenko V.A. Assistant Professor, Candidate of Technical Sciences, Associate Professor at the Department of Electronic Engineering of the “Igor Sikorsky Kyiv Polytechnic Institute”. Author of about 100 scientific publications. His main research interests are developments in the field of microwave electronics, micro- and nanoelectronics.

E-mail: v.kazmirenko@gmail.com, <https://orcid.org/0000-0002-0494-5365>



Poplavko Yu.M. Professor, Doctor of Physics and Mathematics Sciences, Professor of the Department of Microelectronics of the “Igor Sikorsky Kyiv Polytechnic Institute”. Author of about 500 scientific publications. His main research interests are developments in the field of microelectronics, nanomaterials and nanotechnologies.

E-mail: yoplavko@gmail.com, <https://orcid.org/0000-0003-2012-4556>

Kazmirenko V.A.: conceptualization, investigation, validation, analysis, data curation, writing – review & editing.

Poplavko Yu.M.: formulation of the problem, methodology, validation, analysis, data curation, writing – original draft, writing – review & editing.

Термопружна поляризація та інші ефекти у полярних напівпровідниках

С.О. Воронов, В.А. Казміренко, Ю.М. Поплавко

Анотація. Електрична поляризація та пов'язані з нею ефекти зараз набувають значення для електроніки через зростаюче застосування широкозонних полярних напівпровідників, таких як арсенід і нітрид галію. Внутрішня полярність їх структури істотно впливає на втрати міліметрового діапазону, а також на технологічні особливості та застосування електронних пристроїв на основі полярних напівпровідників. Показано, що будь-який п'єзоелектрик має внутрішньо-кристалічний полярний момент, навіть якщо цей кристал не належить до піроелектричної симетрії. Описано новий ефект термопружної поляризації у полярно-нейтральних кристалах; обговорюються деякі можливості його реалізації. Методом часткового обмеження теплових деформацій проведено експериментальне дослідження внутрішньої полярності у п'єзоелектриках. Передбачається, що у технології полярних напівпровідників необхідно враховувати термопружну поляризацію, що дає підстави для створення інтегрованих сенсорів на основі полярних напівпровідників.

Ключові слова: полярні напівпровідники, п'єзоелектрика, піроелектрика, вбудовані датчики.