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Production methods of induced pyroactive structures with functionally significant properties

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The concept proposed for a formation of induced pyroactive structures consists in producing new physical properties in classic piezoelectric crystals under thermodynamically nonequilibrium conditions. External vector action in the form of spatially nonuniform heating of a crystal by incident radiation is proposed for producing new crystalline media with functionally significant properties. Physical principles for creating a new class of pyroelectric sensor devices on the basis of induced pyroactive media are formulated. Sensors with a high upper limit of the dynamic range and devices with the extended functional characteristics are presented in this study.

Предложена концепция получения индуцированных пироактивных структур, заключающаяся в создании новых физических свойств в классических пьезоэлектрических кристаллах с помощью формирования в них термодинамически неравновесных условий. Внешнее векторное воздействие в виде пространственно неоднородного нагрева кристалла излучением используется для создания новых кристаллических сред с функционально важными свойствами. Формулируются физические принципы создания нового класса пироэлектрических сенсорных устройств на основе индуцированных пироактивных сред. Описаны сенсоры с высокой верхней границей динамического диапазона и устройства с расширенными функциональными возможностями.

1. Introduction

The current status of infrared optoelectronics is essentially determined by the quality and variety of the properties of the functional materials involved. Pyroelectric materials hold a central position among them. Owing to their unique physical characteristics as well as the possibility to design new sensor devices on their basis for measurement of temporal and energetic characteristics of electromagnetic radiation, pyroelectric materials are of considerable current use in science and engineering. This paper presents a method of developing induced pyroactive structures on the basis of crystals belonging to the twenty piezoelectric classes. External vector influence in the form of spatially nonuniform heating of a crystal by incident radiation, changing the symmetry of its lattice, induces polarization (the tertiary pyroelectric effect (TPE) [1]) in all noncentrosymmetric crystallographic classes. This effect also becomes possible under uniform heating of a crystal, when there are spatially nonuniform elastic boundary conditions [2, 3]. The presence of thermoelastic stress in a system, resulting in the piezoelectric effect, is a feature common to both heating types.

Among physical effects that involve the polarization response to temperature gradient, the tertiary pyroelectric effect is the most promising for practical applications. The TPE was first used by Ishanin [4], who studied the effect under strain restriction conditions in the plane of the plate. The sensitive element of the radiation detector was an X_1 cut quartz plate rigidly glued to the substrate. We have obtained a number of Author's Certificates [5] on the use of piezoelectric crystals (including nonpolar) as pyrosensitive materials. A possibility to use the TPE for monitoring of high-intensity radiation fluxes was first shown in [6], and for developing multifunctional devices — in [7].

2. Mechanism of the TPE production

Let us consider a crystal in the field of an external perturbation described by a point symmetry group G_{ext}. According to the Curie principle, the crystal symmetry under such an action is determined by the point group G, being simultaneously a subgroup of the symmetry group of the unperturbed crystal G_{cry} and the external action group G_{ext}

$$G \supseteq G_{cry} \cap G_{ext}. \quad (1)$$

Expression (1) must be supplemented with a condition of the relative spatial orientation of the symmetry elements of groups G_{ext} and G_{cry}. The role of this condition in the formation of the group G, describing the symmetry of spatial polarisation distribution in the crystal, is great. There are two factors determining the character of this distribution — the type of the crystallographic cut and the nature of temperature field inhomogeneity in it. A great number of different configurations of the polarization distribution can be obtained by varying these factors for specific problems to be solved.

Under nonuniform heating conditions a crystal is in a thermodynamically nonequilibrium state, which assumes a continuous change in local symmetry. The symmetry group of external influence G_{ext} is spatially inhomogeneous. The temperature field inhomogeneity may considerably vary over small distances, so that the crystal symmetry group in its different regions may be distinct. Under these conditions the Curie principle in the form (1) is inapplicable, because it is impossible to introduce a particular symmetry group of the external influence describing the whole crystal. Under exact statement of the problem, groups G and G_{ext} must define a local symmetry, and the expression (1) written for a local volume must be a local symmetry relationship.

Solution of the equations of state accounting for all types of anisotropy (thermal, electric, optical and elastic ones) for a description of the polarization induced in a crystal by spatially inhomogeneous influence involves severe mathematical difficulties. We elaborated approximate symmetry analysis techniques based on studying one-dimensional nonuniform temperature fields with a temperature gradient directed along the crystal plate thickness or its radius. Temperature fields of this type, being typical in measurements of laser radiation parameters, produce polar states which can be analyzed by symmetry relationship (1).

Let us consider a mechanically free plate under nonuniform heating. To describe a polar state in an isolated local volume V_0, we can use expansions for the thermodynamic potential [8]. Then, the linear polarization response in the approximation of the quasiequilibrium crystal state may be put down as follows

$$\delta P_i(r,t) = d_{i\lambda} C_{\lambda\nu} \alpha_\nu \theta(r,t) + d_{i\lambda} \sigma_\lambda(r,t), \quad (2)$$

where coefficients $d_{i\lambda}$, α_ν, σ_λ are the piezoelectric tensor components, thermal expansion tensor components, and thermoelastic stress tensor components, respectively; $C_{\lambda\nu}$ are the elastic stiffness constants, $\theta(r,t) = T-T_0$ is the crystal temperature increment, T_0 and T are the initial and final temperatures. The relationship (2) defining the piezoelectric contribution to polarization is exact under uniform crystal heating. Under nonuniform heating, σ_λ and θ should be regarded as local values of stress and temperature, with relationship (1) becoming applicable to the local volume V_0, in which the tensor σ_λ is constant and can be approximated by group G_{ext}.

The first term in (2) corresponds to free thermal expansion of the volume V_0. It describes the contribution of the secondary pyroelectric effect to local polarization, whose quantity is determined by properties of the crystal only. The secondary pyroeffect symmetry is the symmetry of the polar vector coinciding with a unique polar direction, if such a direction is present in the unperturbed crystal (otherwise, this contribution is equal to zero). The second term defining the TPE describes the piezoelectric effect caused by thermoelastic stresses acting from the environment on the volume V_0 and deforming this volume to its real value. The TPE symmetry is determined in accordance with (1) by the symmetry of the tensor σ_λ. It is fundamentally distinguished from the secondary pyroeffect symmetry, resulting in the existence of TPE in the crystals not belonging to the polar classes.

3. Symmetry of induced polar states

3.1. *Surface heating.* Let us consider symmetry properties of a spatial polarization distribution under surface absorption conditions, when the temperature gradient is perpendicular to the plane of the plate. Thermoelastic fields are self-balanced in the absence of surface loads [9]. As a consequence, the thickness-averaged tertiary polarization component is zero

$$<d_{i\lambda}\sigma_\lambda(r,t)> = 0. \tag{3}$$

Therefore, TPE-based devices require a new approach for detecting the electric signal of the sensitive element, since the methods used in conventional pyroelectric sensors average the polarization in the sample volume. Equation (3) is a consequence of the mechanical state of the plate defined by its bending. The plate volume is divided into three layers, each characterized by a plane stress state. The symmetry group describing this state is ∞/mmm (infinite-fold rotation axis is normal to the plane of the cut; m is the mirror plane of the limiting group, coinciding with the planes of the plate and layer). I.e., the thermoelastic stress tensor $\sigma_\lambda(r,t)$ in the layer is invariant to the transformations of this group. In such a manner the symmetry group of the external influence may be put down as follows

$$G_{ext} = \infty/mmm, \quad C_\infty \| \mathbf{n}, \tag{4}$$

where **n** is the normal to the plate, C_∞ is the infinite-fold axis. In order to determine the cuts (given by the vector **n**) in any crystallographic class that are active with respect to the TPE manifestations, one should substitute relationship (4) into (1). Bending of the plate caused by grad T is accompanied by the appearance of unipolar regions in it. The signal detection from these regions and organization of these signals into measurement channels operating in an independent mode allows the development of TPE-based multifunctional devices. One such instrument is a watt/joule meter, which provides for simultaneous pulse power and energy measurements using one sensitive element. The watt/joule meter was first developed on the nonpolar cuts of a $LiNbO_3$ crystal [7]. This paper examines new functional capabilities of quartz as an induced pyroelectric response material.

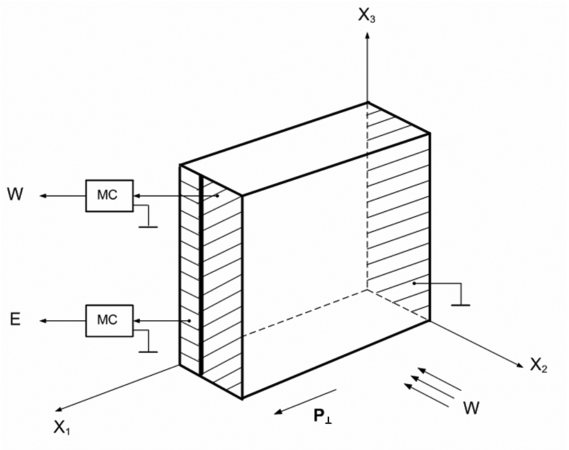

Fig. Pyroelectric watt/joule meter based on the X_2 cut quartz. (MC) matching cascades for the power (W: $\sigma_e <<|\sigma_p$) and energy (E: $\sigma_e > \sigma_p$) measurement channels; τ_e is the electric time constant, τ_p is the pulse duration.

Let us use relationships (1) and (4) to find pyroactive cuts of quartz. In cuts normal to any one of the equivalent axes C_2 or parallel to them, the symmetry group $G = C_2$. There are the longitudinal TPE ($\mathbf{P}\|\mathbf{n}$) in the first case and transverse one — in the second. Under the assumption made (3) the longitudinal TPE in radiation measurements, using an electrode system in the form of a flat capacitor, may not be applied. The transverse TPE (namely, the X_2 cut) was found to be a suitable effect for measuring purposes. The tertiary polarization component coinciding with the X_1 axis direction is generated in the plane of the X_2 cut quartz

$$P_1(y) = \tag{5}$$
$$= d_{11}(\alpha_1 S_{33} - \alpha_3 S_{13})(S_{11}S_{33} - S_{13}^2)^{-1}\Psi\{\theta(y)\},$$

where $\Psi\{\theta(y)\} = 12y<y\theta(y)> l^{-2} + <\theta(y)>-\theta(y)$, l is the plate thickness, y is the coordinate along the X_2 axis, $S_{\lambda\nu}$ are the elastic compliance constants. The polarization distribution (5) enables a multifunctional sensor to be developed. Two electrodes isolated from one another, covering regions of a crystal surface with bound charges that are identical in sign, have to be deposited on the face plate normal to the induced unique polar direction. A continuous electrode is deposited on the opposite face. Each of the electrodes must be connected to a corresponding matching cascade, forming two independent channels for pulse power and energy measurements in this fashion (Fig.).

3.2. *Radial heating.* High-intensity radiation measurements (>1 kW) require a considerable increase in the measurement range of energetic characteristics. This becomes available using the TPE in crystals that do not belong to the central crystallographic classes and are characterized by high transmission at the detection wavelength, stable characteristics, high radiation hardness. Unique electrophysical characteristics of quartz and zinc selenide make it possible to apply them as pyroactive materials in the visible and near-IR spectral regions for transmission-type pyroelectric sensors. These devices can be considered as multifunctional optical elements, which combine the functions of output laser windows and meters of their energetic parameters. A sensor of this type was first developed on the basis of the [111] cut of a ZnSe crystal [6].

Let us consider axisymmetric heating by radiation with a wavelength in the transmission band of the crystal. The temperature field produced by the periodic component of a sine-modulated beam is a quasistationary field with two regions: heated and cold. These zones are separated by a narrow layer of thickness of the order of the temperature wavelength λ_T. The symmetry of the polar states in the heated region of the crystal ($r \le r_0$) defined by a laser beam of radius r_0 is the same as under surface heating. The reason is that the mechanical state of the heated crystal region approaches the absolute clamping in the plane of the plate. Therefore, the external influence is characterized by the cylinder symmetry ∞/mmm.

The cold crystal region ($r>r_0$) is under highly inhomogeneous influence: a loaded inside boundary of the region and a free outside surface. There is a strong radial dependence of the angular components of the thermoelastic stress tensor σ_λ across the boundary between regions. These components change sign over a distance of the order of λ_T. Under such conditions, group G_{cry} retains only the rotation axis n (if it is normal to the plane of the cut) and the symmetry plane m (if it coincides with the plane of the cut). When no the indicated symmetry elements exist in G_{cry}, the group G_{ext} is represented by the trivial symmetry group I, and the TPE will be developed under dissymmetry conditions only:

$$G_{ext} \supseteq \begin{cases} n/m, \text{ if } n \text{ and } m \subset G_{cry} \\ I, \text{ if } n \text{ and } m \not\subset G_{cry} \end{cases}. \qquad (6)$$

Let us consider a X_3-cut quartz. Since the piezoelectric effect is rigorously forbidden along the C_3 axis, then there is no the longitudinal TPE in the whole plate volume. In the cold region in accordance with (6) the polar state is characterized by the symmetry group $G = 3$, however the transverse TPE takes place. Group $G = 3$ fulfils its function — the polar state existing in the X_1X_2 plane, is invariant to the symmetry elements of this group. Numerical calculations and experiments have revealed that the angular distributions of the radial polarization component and bound charge on the lateral surface of the plate are proportional to sin 3α. Therefore, the electrode configuration on the sensitive element of the sensor defined by symmetry of the transverse effect is similar in design to that described in [6]. The upper limit of the dynamic range of this sensor reaches 1.5 kW/cm^2, its sensitivity is equal to $(2\div5)\cdot10^{-2}$ V/W. It should be noted that we had also developed longitudinal TPE-based sensors on a ZnSe crystal (the [111] cut) and quartz (the X_1 cut) [10].

4. Conclusions

External vector action in the form of spatially nonuniform heating of a crystal by incident radiation is proposed as alternative method for producing induced pyroactive structures on the basis of crystals belonging to the 20 noncentrosymmetric crystallographic classes. This approach considerably extends the class of pyroelectric materials possessing the required optical, electrical and thermoelastic properties for their use in functional optoelectronics.

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Методи формування індукованих піроактивних структур з функціонально важливими властивостями

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Запропоновано концепцію одержання індукованих піроактивних структур, що полягає у створенні нових фізичних властивостей у класичних п'єзоелектричних кристалах за допомогою формування у них термодинамічно нерівноважних умов. Зовнішній векторний вплив у вигляді просторово неоднорідного нагрівання кристала випромінюванням використовується для створення нових кристалічних середовищ із функціонально важливими властивостями. Формулюються фізичні принципи створення нового класу піроелектричних сенсорних пристроїв на основі індукованих піроактивних середовищ. Описано сенсори з високою верхньою границею динамічного діапазону і пристрої з розширеними функціональними можливостями.