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The Photovoltaic and Photorefractive Effect in Cubic Zns Crystals

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Abstract
Background: In the present work, the photovoltaic and photorefractive effects are discovered and studied and the only nonzero photovoltaic coefficient k_{ijk} was determined for a cubic ZnS crystal. This coefficient $K_{14} = 2\cdot10^{-9} A\cdot cm\cdot(W)^{-1}$. The coefficients k_{ijk} exceed the corresponding coefficients in LiNbO3:Fe by more than an order of magnitude.
Objectives: The paper presents the results of a study of the volumetric photovoltaic effect in piezoelectric ZnS crystals belonging to the cubic point group m. The possibility of using photopiezoelectrics in the holographic recording is shown.
Methods: The use of photopiezoelectrics in holographic recording offers advantages. In this case, the recording is carried out by two coherent beams with polarization corresponding to the photovoltaic current. When reconstructing the recorded hologram is achieved by illuminating the crystal with a beam of coherent light of the same wavelength.
Conclusions: However, the polarization of this beam is chosen so that the illumination does not lead to the generation of photovoltaic current. Erasure of the recorded hologram is achieved by uniformly illuminating the surface with a beam of light from the previous polarization.

Keywords: the volumetric photovoltaic effect, cubic ZnS crystal, the anomalous photovoltaic effect, polarization.

1. Introduction

Photo-EMF (or photovoltage) in semiconductors, regardless of its nature, cannot exceed the band gap, i.e. a few volts. For example, in a homogeneous semiconductor, the Dember (diffusion) photovoltage for an arbitrarily high intensity of the exciting light does not exceed the value [1]

$$V = \frac{KT}{q} \ell n \frac{n_1}{n_0} << \frac{KT}{q} \ell n \frac{N_c}{n_0} = E_g, \qquad (1)$$

Where E_g is the semiconductor band gap, n_1 and n_0 are the nonequilibrium and equilibrium carrier concentrations, respectively, and N_c is the density of states.

Another example is the photovoltage that occurs when the pn-junction is illuminated [2].

$$V \leq \frac{KT}{q} \ell n \frac{n_n p_p}{n_0{}^2} = E_{Fn} - E_{Fp}, \qquad (2)$$

which also does not exceed E_g. Here n_n and p_p are, respectively, the concentrations of electrons in the *n*-region and holes in the *p*-region. E_{Fn} and E_{Fp} are the energies of the Fermi level in the *n*- and *p*-regions.

The exception to this rule was only semiconductor textures in which the effect of anomalously large photovoltages (APV effect) is observed, due to the addition of elementary photo-EMFs of Dember (1) or elementary photo-EMFs (2), developing on individual *p*-*n*-junctions of the texture [3].

In such textures of sawn layers of CdTe, Ge, Si, GaAs, PbS, CdSe, etc., photovoltages can reach values on the order of several hundred volts per centimetre of length in the direction of the addition of elementary photo-EMFs (1) or (2).

In recent years, it has become clear that currents of a different nature are possible under thermodynamic nonequilibrium conditions, due to the absence of a medium of a centre of symmetry. The most important of this class of effects is the anomalous photovoltaic effect (APV effect).

2. Objectives

The AF effect consists in the fact that, under uniform illumination of a short-circuited ferroelectric, a stationary current flows through it, which was called photovoltaic in [4, 5]. It was shown that it is the photovoltaic current that leads to the anomalous photovoltaic effect (APV effect) in a ferroelectric.

The anomalous photovoltaic effect, discovered for ferroelectrics for the first time in [4, 5], is a special case of the AF effect, which is described for crystals without a centre of symmetry by a tensor of the third rank α_{ijk} [5,6]:

$$J_i = \alpha_{ijk} E_j E_k^* \quad (3)$$

According to (3), under uniform illumination of homogeneous crystals without a centre $J_i = \alpha_{ijk} E_j E_k^*$ of symmetry (ferroelectric, pyro, or piezoelectric crystal) with linearly polarized light, a photovoltaic current Ji arises in it, the sign and magnitude of which depend on the orientation of the light polarization vector with projections E_J, E_K^*.

Tensor Components$\alpha_{\mathrm{ijk}}$are nonzero for 20 acentric symmetry groups. If the crystal electrodes are opened, then the photovoltaic current J_i generates photovoltages $U_i = \frac{J_i}{\sigma_T + \sigma_p} l$, where σ_T and σ_p dark and photoconductivity, respectively, l distance between electrodes. The generated photovoltage is about 103-105V, exceeding the band gap E_g by two to four orders of magnitude.

In accordance with (3) and the symmetry of the point group of the crystal, we can write expressions for the photovoltaic current J_i. Comparison of the experimental angular dependence J_i (β) with (3) allows you to determine the photovoltaic tensor a_{ijk} or the photovoltaic coefficient $K_{\mathrm{ijk}} = \frac{1}{\alpha *} \alpha_{\mathrm{ijk}}$ (a* - light absorption coefficient).

3. Methods

3.1. Photovoltaic effect in piezoelectric ZnS crystals. The paper presents the results of a study of the volumetric photovoltaic effect in piezoelectric ZnS crystals belonging to the cubic point group $\bar{4}3$ m.

Cubic ZnS crystals grown by the hydrothermal method in H_3PO_4 and KOH solutions were studied at the Laboratory of Hydrothermal Synthesis of the Institute of Crystallography of the Russian Academy of Sciences.

In contrast to ferroelectrics [4, 5], the photovoltaic effect in ZnS can only be observed in polarized light [8, 9]. In accordance with (3) and the symmetry of the point group, when the crystal is illuminated in the z direction of the 4th order axis (*z*-axis), the expression for the photovoltaic current in the z direction has the form:

$$J_Z = \frac{1}{2} \alpha^* K_{14} I \sin 2\beta, \quad (4)$$

where β is the angle between the plane of polarization of the light and the *x*-axis.

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Measurement of the photovoltaic current Jz and the field it generates $\tilde{E} = \frac{J}{\sigma_p}$ (σ_p - photoconductivity) was carried out by taking stationary current-voltage characteristics [5].

Figure 1 shows the orientation dependence $J_z = J_z(\beta)$ in the [001] direction taken at T = 143K under illumination with light with a wavelength l=500 nm (α*=5 cm-1) and intensity I=2.3·10^{-3} W·cm^{-2}. The crystal is illuminated by plane polarized light in the [001] direction. A comparison of this angular dependence with (4) gives

K_{14}=2·10^{-9}A·cm·$(W)^{-1}$.

Thus, the value of the K14 modulus in the studied ZnS crystals is significantly higher than that of known ferroelectric and piezoelectric materials [4, 5, 6].

In the range T=140-300 ^{0}K, the K_{14} module exhibits a weak temperature dependence. Due to this, and also due to the strong temperature dependence of the photoconductivity σ_p, the field generated in the direction of the *z*-axis $\tilde{E} = \frac{J}{\sigma_p}$ varied from 1V cm^{-1} (T=300 ^{0}K) to 40V cm^{-1} (T=143 ^{0}K) and did not depend on the light intensity *I*.

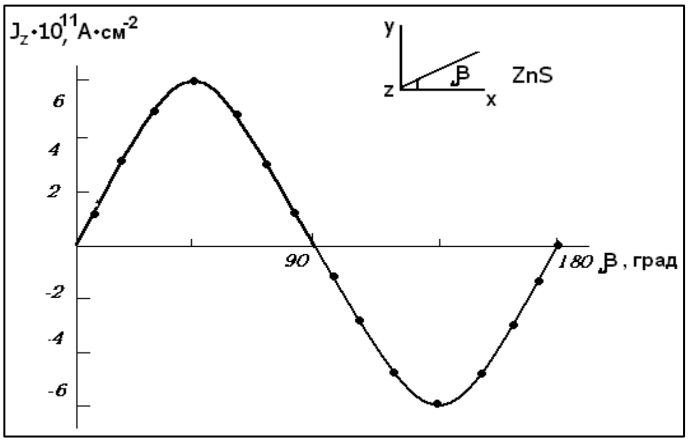

Figure 1. Orientation dependence of the photovoltaic current density Jz in the [001] direction. (T=143K, I=2.3·10^{-3} W·cm^{-2}, λ=500 nm).

In ZnS crystals grown by the hydrothermal method, the photovoltaic effect is mainly of an impurity nature. This can be seen in Fig. 2, which shows the spectral distributions of the photoconductivity σ_p (1) of the photovoltaic current (2), referred to as the units of the incident energy and the optical absorption edge (3).

Impurity band in the spectral distribution$J_z$takes place near λ=500 nm. The impurity maximum of photoconductivity is also located there. For crystals grown in an acidic or alkaline medium, the impurity maximum has a different position and shifts within 450–500 nm.

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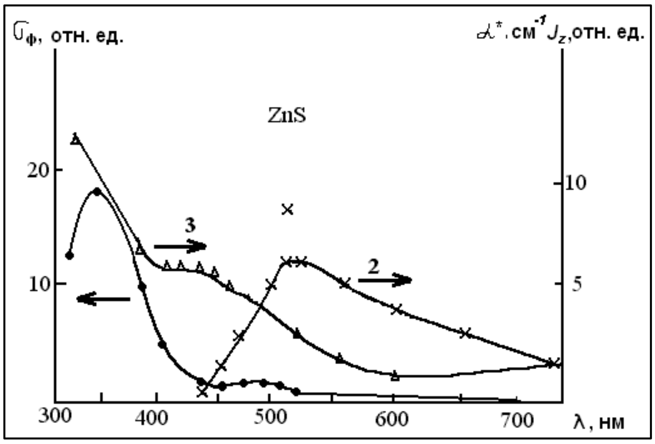

Figure 2. Spectral distribution of photovoltaic current J_z (2), photoconductivity σ_p (1) and optical absorption α * (3) whenT=143K. β=45°.

3.2. Photorefractive effect in cubic ZnS crystals. The influence of nonequilibrium carriers on the birefringence of ferroelectric and piezoelectric crystals has been called the photorefractive effect (PR effect) in the literature and has found wide use for recording volume holograms. The PR effect is as follows. As a result of local illumination or a piezoelectric crystal with intense transmitted light (a focused laser beam), a reversible change in birefringence takes place in the volume of the crystal inside the light beam, mainly due to a change in the refractive index of the extraordinary beam ne. The magnitude of this change reaches 10^{-4} -10^{-3} for some pyroelectrics ($LiNbO_3$ $LiTaO_3$), and its lifetime can vary over a wide range, from milliseconds in $BaTiO_3$ to months in $LiNbO_3$. The hologram is recorded due to the volumetric modulation of the value Δn, corresponding modulation of the recording beam. Recording resolution is exceptionally high, 10^2-10^4 lines/mm. [7-15].

4. Results

The main advantage of this optical memory method compared to photographic layers is the possibility of parallel writing, reading and erasing.

As shown, the sign and magnitude of the photovoltaic current depend on the symmetry of the crystal and the polarization of the light. The photovoltaic current leads to the generation of anomalously large photovoltages in the same direction. Thus, during the exposure time *t*, a macroscopic field arises in the crystal $\tilde{E}$.

$$\tilde{E} = \frac{4\pi}{\varepsilon}\int_0^t J dt \, , \quad (5)$$

Due to the linear electric effect, the field $\tilde{E}$ leads to the PR effect:

$$\Delta n = \frac{1}{2} n_i^3 r_{ij} \tilde{E} \, , \quad (6)$$

where r_{ij} are the electro-optical coefficients. Equation (6) is written in the head coordinate system. After lighting the field $\tilde{E}$ remains in the crystal for a long time due to the capture of nonequilibrium electrons and holes. This capture mechanism is responsible for optical memory. Erasing can be done by annealing the crystal at 17 °C. There are other methods of erasing.

In high-resistance ZnS crystals, one can observe the PR effect, the sign and amplitude of which depend on the orientation of the light polarization plane (4) Fig.1. The use of photopiezoelectrics in holographic recording offers advantages. In this case, the recording is carried out by two coherent beams with polarization corresponding to the photovoltaic current J_z and the field E_z in the *z*-direction ($\beta = 45^0$). Reconstruction of the recorded hologram is achieved by illuminating the crystal with a beam of coherent light of the same wavelength. However, the polarization of this beam is chosen so that the illumination does not lead to the generation of photovoltaic current in the z-direction ($\beta = 90^0$). Erasure of the recorded hologram is achieved by uniformly illuminating the surface with a beam of light from the previous polarization ($\beta = 45^0$). Thus, the use of light in different directions of the polarization plane makes it possible to reconstruct a hologram recorded in a photopiezoelectric without noticeable damage. Figure 3 shows the holographic recording, recovery, and erasing of a recording in a photopiezoelectric.

Also, the AP effect in crystals without a centre of symmetry can be applied as a new type of photovoltaic energy converter element. The efficiency of converters of light energy into electrical energy based on the photovoltaic effect of the pack is low.

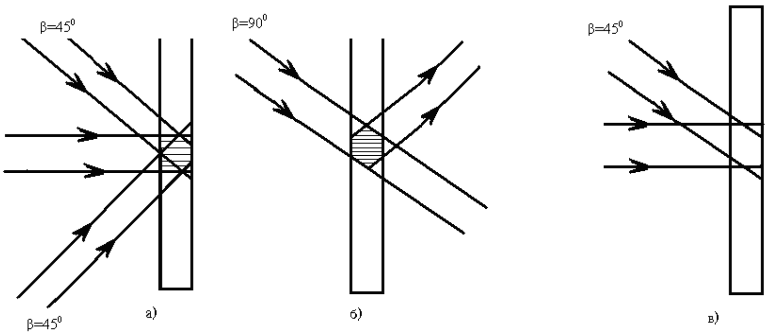

Figure 3. Holographic recording in photopiezoelectrics
a) Recording of an elementary hologram; b)recovery; c) deletion of the record.

However, ferroelectric, and ipezoelectric materials can be used to generate low power reference voltages. At the same time, the spectral sensitivity of these elements varies over a wide range: from the vacuum ultraviolet to the red visible region.

There are opportunities to apply these processes in silver-free photography and vidicons, as well as in nanotechnology.

5. Conclusion

The photovoltaic and photorefractive effect was discovered and studied and the only non-zero photovoltaic coefficient is determined

$K_{14} = 2\cdot10^{-9}$A cm$\cdot$(W)$^{-1}$for a cubic ZnS crystal. The coefficients K_{14} are more than an order of magnitude higher than the corresponding coefficients in $LiNbO_3$:Fe.

The possibility of using photopiezoelectrics in the holographic recording is shown. In this case, the recording is carried out by two coherent beams with polarization corresponding to the photovoltaic current. Reconstruction of the recorded hologram is achieved by illuminating the crystal with a beam of coherent light of the same wavelength. However, the polarization of this beam is chosen so that the illumination does not lead to the generation of photovoltaic current. Erasure of the recorded hologram is achieved by uniformly illuminating the surface with a beam of light from the previous polarization. Also erasing can be done by annealing the crystal at 17℃.

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