Photo-induced effects in the doped ferroelectric

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Abstract. Light induced currents in thin lithium niobate crystal were described. New effects were observed in doped lithium niobate crystals with two electrodes of different metals (sandwich system). The light induced response includes the photovoltaic effect and the thermoinduced effect. Spectral and coordinate dependences of the light response are investigated.

1. Introduction
The photovoltaic effects are well known phenomena for the ferroelectric crystals [1-3]. Last time were discovered a series of nonequilibrium phenomena in ferroelectrics, which do not have a definite theoretical description [3,4]. In paper [5] the thermoinductive effect consisting in initiation of the electric voltage between the opposite faces of the semiconductive sample of samarium sulphide (SmS) on heating to 400–500 K is described. The effect has appeared in the presence of the donor impurity concentration gradient directed towards these faces.

In this paper, the results obtained in experimental studies of the light induced currents in the thin-layer metal-lithium niobate-metal (MLM) structure are presented. The spectral and coordinate dependences of the light response are experimentally investigated. This effect is similar to photovoltaic effect, but it includes the thermal contribution. The possible models of the investigated phenomena are discussed.

2. Spectral dependence of the light induced response
The samples of doped lithium niobate crystals (iron concentration is equal to 0.3 wt%) with different pairs of electrodes were studied. The metal electrodes were applied by vacuum evaporation with thickness varying from 0.1 to 1 μm. The samples with different pairs of electrodes (Al – Cr, In – Cr, Al – Cu, Ag – Al) were used.

The study of the light induced effect was performed using the slow modulation of the light falling on the crystal. Because the sufficiently high rates of heating [about 0.1 K/s] were registered during the experiments, the pyroelectric current for the polar Z-cut crystals reached the considerable value. Therefore, the principal measurements were performed for the Y-cut lithium niobate crystals where the pyroelectric response could be observed in pure form.

It was experimentally measured the coefficient characterizing the light induced response:

\[ G = \Delta U_n / P, \ (V/W), \]  

(1)
where $\Delta U_n$ is the change of voltage across load impedance $R_n$ when the sample is illuminated by the light, $P$ is the power of the incident radiation.

The measurement results are presented in Figure 1. It was used the LiNbO$_3$:Fe crystal (0.3 wt.% Fe, Al–Cr, $2 \times 2.5 \times 0.13$ mm$^3$). The preamplifier coefficient is $K=20$. The light response has a sharply defined spectral dependence with sign changing about 0.9 $\mu$m wavelength.

![Figure 1](image_url)

**Figure 1.** The photocurrent coefficient versus the radiation wavelength: a – the translucent electrode; b – the blackened absorbing electrode

The calibration measurements revealed a very weak (a few percent) spectral dependence of absorptive electrode. It can be concluded that the sharp spectral dependence of the light response is due to the bulk absorption in the crystal, because the electrodes are partially transparent. The presence of volumetric absorption suggests that changing of the signal character and its growth toward the short waves are induced by the fotogalvanic effect. The evaluation of Glass constants (in the field 0.5÷1.5 $\mu$m) is consistent with data available in the literature [3]. It can be assumed that the response in the infrared spectrum region is due to the thermovoltaic effect.

### 3. Thermovoltaic effect in the metal-ferroelectric-metal sandwich structure

In our work [6], the thermally stimulated quasi-stationary current arising only in the highly alloyed with iron crystal of lithium niobate with the evaporated electrodes from a pair of different metals was described. A sign of the therminduced electro-moving force (EMF) is determined by location of electrodes applied by vacuum evaporation on the opposite faces of crystal and does not depend on orientation of the crystallographic axes of the sample in reference to electrodes.

In contrast with the classic pyroelectric effect, the value of observed thermal response is proportional to the crystal temperature increase and does not depend on the rate of its change. It was experimentally measured the coefficient characterizing the thermo-EMF value in the mode of voltage $U_n$ measurement:

$$P_{el} = (R_n S)^{-1} \Delta U_n / \Delta T, \text{ (A/K-cm$^2$)}$$

(2)
where $S$ is the area of crystal surface covered with sputtered (evaporated) electrode; $\Delta U_n$ is the change of voltage across load impedance $R_n$ when the sample temperature changes by $\Delta T$; $\Delta T$ is the difference between the initial and final temperatures of sample [6].

The study of the effect was performed using the slow modulation of the crystal temperature under the conditions of thermostat and the thermo-EMF was recorded under the stationary conditions (relaxation was not observed for observation time $\tau \approx 10^5$ s). The measurements showed that the thermo-voltaic effect has approximately equivalent values in the Y- and Z-cut crystals. Because the sufficiently high rates of heating [about 0.1 K/s] were used in the installation, the pyroelectric current for the polar Z-cut crystals reached the considerable value. Therefore, the principal measurements were performed for the Y-cut lithium niobate crystals where the thermal response could be observed in pure form.

The metal electrodes were applied by vacuum evaporation with thickness varying from 0.1 to 1 $\mu$m. The samples with different pairs of electrodes were studied. For studying the dependence of the thermo-EMF value on the concentration of impurity, the lithium niobate crystals with the same areas and thicknesses [$S = 0.5$ $cm^2$, $d = 1$ mm] were used. The iron concentration varied in the range of $1.3 \cdot 10^{-2}$ wt% to 0.6 wt%. For the impurity concentration of less than 0.25 wt%, the thermo-voltaic effect is not observed. Beginning with the impurity concentration of 0.25 wt%, the coefficient $P_{el}$ rises sharply and reaches maximum ($P_{el} = 5 \cdot 10^{-12}$ A/cm$^2$K) at concentration of $0.3 \div 0.4$ wt% of Fe.

When investigating the dependence of the coefficient $P_{el}$ value on the sample geometry, it was identified that $P_{el}$ value increases sharply when the crystal thickness decreases (Figure 2).

$P_{el}, 10^{-10} A \cdot K^{-1} \cdot cm^{-2}$

$L, 10^{-4} \text{ mm}$

Figure 2. The coefficient $P_{el}$ versus the crystal thickness ($S=5$ mm$^2$; 0.3 wt% of Fe; Al–Cr electrodes.

The known contact phenomena in the sandwiched structures with ferroelectrics do not explain the observed quasi-stationary currents [7,8]. The presence of initial voltage $U_n^0$ across the sample allows us to suggest the non-equilibrium nature of the thermally stimulated current. In our work [9] it was proposed the electret model of the MLM structure. In this model, the thermoinduced changing of the conductivity of the crystal leads to change in the stationary current on the load impedance [10].

4. Coordinate dependences of the light induced response

In experiments using as the source of radiation He-Ne laser (0.63 $\mu$m) it was revealed the dependence of light induced response from the coordinates of the laser spot on the crystal top surface (Figure 3).

The crystal was installed in the coordinate table, which allows you to seamlessly move crystal in two directions. The light spot diameter in the focus lens was 340 $\mu$m.
The value of the stationary light response versus X (along polar axes) and Y-coordinates is shown in Figure 4a. The coefficient $G^*$ ($G$ in arb. un.) reaches the greatest magnitude at the ends of the crystal and it takes different signs at the opposite ends of the sample. This asymmetry can be associated with only one selected direction in crystal associated with the polar axis X. The coefficient $G^*$ versus Y-axis is changed monotonically (Figure 4b).

The anomaly in the coordinate dependence can be explained by the existing two response mechanisms (photovoltaic and thermovoltaic) with different signs. The photovoltaic response gives the contribution of light induced current, because the electrodes were partially transparent. This is confirmed by the next experimental fact. When the upper electrode was blackened this coordinate dependence disappears. The detail explanation of the describing experiments requires the next investigations.

5. Conclusions
The results obtained in experimental studies of the light induced currents in the thin-layer metal-lithium niobate-metal structure are presented. In the nonsymmetrical MLM system is registered the stationary light induced current. The light response has a sharply defined spectral dependence with sign changing. In experiments with the local illumination of the LiNbO$_3$:Fe crystal it was revealed the anomalous dependence of light induced response from the coordinates of the laser spot on the crystal top surface. The alleged explanation of the both effects includes the photovoltaic effect and the theromovoltaic contribution.
The results obtained can be used for investigating the properties of the sandwiched ferroelectric structures [11-13] as well as for developing new types of the photo-electrical energy converters [14-16].

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