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Features of H_2O adsorption on a polar surfaces of $LiNbO_3$ crystals

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The features of the surface electrical conductivity of a series of $LiNbO_3$ crystals of different compositions are studied. It is shown that when the crystals are cooled, H_2O molecules are adsorbed and dissociated on their polar surfaces, and the intensity of this process depends on the unipolarity of the sample.

Keywords: lithium niobate, electrical conductivity, adsorption, H_2O.

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1. Introduction

It is well known that the presence of water adsorbed from the air on the surface of many high-resistance dielectric materials can result in a noticeable surface electric conductivity [1,2]. This effect should be most explicitly manifested in ferroelectrics because their polar surfaces almost always have foreign charges that are involved in the process of depolarization field screening [3].

Ferroelectric materials find a very wide application in the modern microelectronics, acoustoelectronics and optoelectronics, and one of the most demanded ferroelectric material is lithium niobate (LN) $LiNbO_3$. The issues of adsorption and desorption of H_2O molecules on polar surfaces of $LiNbO_3$ crystals have been discussed in a number of theoretical studies [4–7], however, there is an obvious lack of experimental investigations of the surface conductivity in LN crystals.

Probably the first mention of the adsorption of H_2O molecules by polar surfaces of LN crystals and its strong effect on the surface electric conductivity can be found in [8]. Also, in the studies of electrical properties of LN and $LiTaO_3$ crystals the effect of reduced resistance of samples in the temperature region of $(300-400)$ K has been noted. This effect disappeared only after the sample heating up to a temperature of ~ 450 K followed by cooling in the presence of pre-dried silica gel [9,10]. This has opened the way to explain the effect of resistance reduction by the initial presence of dissociated molecules of water on the crystal surface which resulted in the emergence of a strong surface conductivity.

The purpose of this study is to investigate electrical properties of the conductive layer that is formed on the surface of LN crystals due to adsorption and subsequent dissociation of water molecules. This allows evaluating the adsorption features of LN crystals with different compositions and states.

2. Samples and study methods

Three z-cut plates of LN crystal with sizes close to each other were selected as samples. The set included a nominally undoped sample of congruent composition (CLN) and two samples grown from the congruent melt with addition of 2.0 mol% and 7.0 mol% of MgO (in the charge). The synthesis was carried out by the Czochralski method. The $\sigma_z(T)$ dependence of specific conductivity on temperature along the z direction was investigated earlier for all samples [11]. The information about samples is given in Table 1. The table also contains calculated currents through the crystal I_{calc} for one of the experiment implementations (see below).

The main series of experiments was carried out as follows. On one of pairs of opposite nonpolar faces of the samples electrodes made of the In$-$Ga eutectic were applied. One of the electrodes is either connected to a controlled stabilized high-voltage source or grounded, and the second electrode is connected to the input of an electrometric amplifier with an input resistance of 1.08 GΩ. With this connection the electrical resistance of the sample is a parallel connection of the crystal resistance R_c and the resistance of the surface adsorbed layer R_s. The surfaces free from electrodes were polished to optical quality and degreased by isopropyl alcohol. Before proceeding with measurements, the samples were held in a thermostating module for at least 20 hours at a relative air humidity of $(62 \pm 5)\%$ and at room temperature. Humidity was monitored by a calibrated analog sensor of HIH-4000 type (Honeywell) and corrected, if necessary.

To measure the primary pyroelectric coefficient, electrodes were applied on polar surfaces of samples and measurements were performed by the quasistatic method with continuous variation of sample temperature at a known rate V [12]. All measurements were carried out using the same equipment as in [11].

Table 1. Some characteristics of studied crystals

	Composition	Dimensions, mm			σ_z, $(\Omega \cdot \mathrm{cm})^{-1}$ at $T = 300\,\mathrm{K}$	Ref	I_{calc}, fA at 300 K	R_s, Ω (calc.)
		x	y	z				
$S1$	CLN	5.89	6.01	3.62	$(7.8 \pm 0.6) \cdot 10^{-17}$	[11]	~ 2.7	$\sim 2 \cdot 10^{15}$
$S2$	LNMg (2.0 mol.%)	5.72	5.95	3.68	$(3.3 \pm 0.6) \cdot 10^{-17}$	[11]	~ 1.3	$\sim 2 \cdot 10^{8}$
$S3$	LNMg (7.0 mol.%)	6.22	5.45	3.48	$(2.0 \pm 0.4) \cdot 10^{-17}$	[11]	~ 0.8	$\sim 10^{15}$

3. Experimental results and discussion

First the time dependence of the current through the sample at a fixed (room) temperature and a fixed relative air humidity $(62 \pm 5)\%$ was studied. The sample was supplied with a direct voltage of $U = 100\,\mathrm{V}$ via an integrating RC-circuit (with a time constant of $\tau = 32\,\mathrm{s}$). The corresponding dependencies for samples $S1$ and $S2$ are shown in Fig. 1.

The corresponding dependence obtained for sample $S3$ is qualitatively similar to that for sample $S1$, but the steady-state current through the sample measured 60 min after the connection of the voltage source was equal to (105 ± 10) fA. It can be seen that the initial section of the time dependence of current through sample $S1$ corresponds to the classical transient process for differentiating RC-circuit. It is worth noting that values of the steady-state bulk conduction current I_{calc} (see Table 1) calculated in the approximation of electric conductivity isotropy are considerably less than the experimentally measured values. This is indicative of the presence of a significant surface conductivity in all three samples. Evaluations of R_s are shown in Table 1 as well.

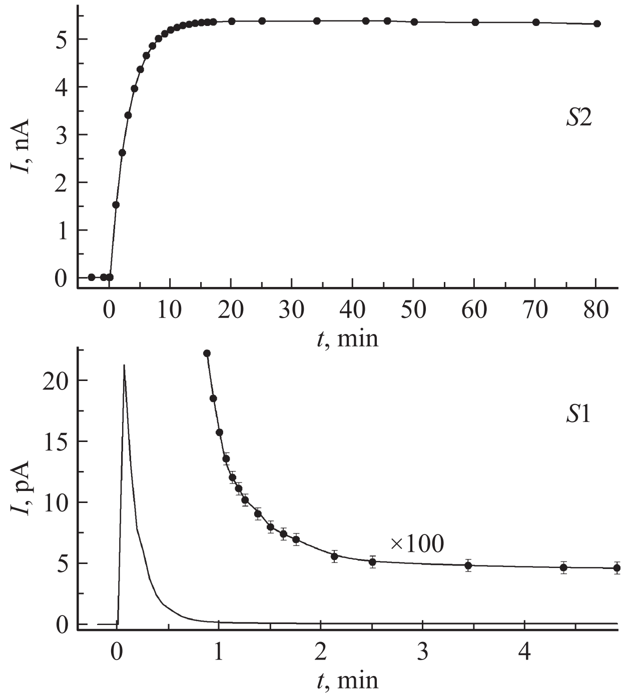

Figure 1. Time' dependence of current for samples $S1$ and $S2$ at a fixed (room) temperature.

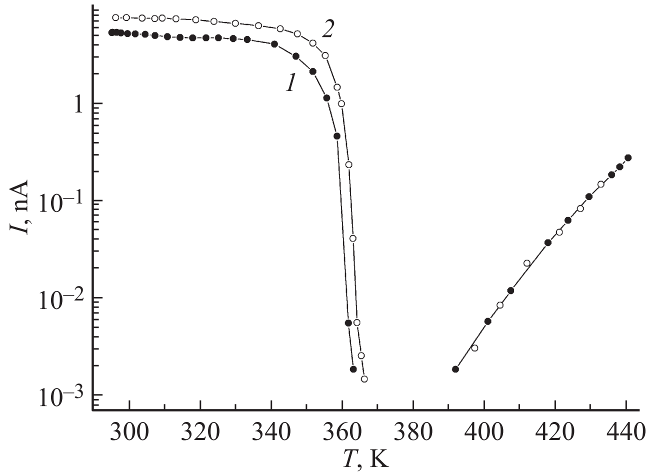

Figure 2. Two typical implementations of the temperature dependence of current through sample $S2$.

The surface conductivity of sample $S2$ at room temperature stands out sharply against two others with almost time-independent current through the sample after the end of the transient process. Therefore, the main attention in further experiments has been focused exactly on this sample.

Very representative results were obtained from the measurement of temperature dependence of current through sample $S2$ in the same experiment configuration at $U = 100\,\mathrm{V}$. The experiment was carried out multiple times in the same mode of sample heating and is characterized by a rather good repeatability of results. Typical $I(T)$ dependencies for two implementations of the experiment are shown in Fig. 2.

The I_0value in different implementations of the experiment at room temperature and at $U = 100\,\mathrm{V}$ was in the range of $(4-10.5)$ nA, and the temperature T_e at which the current through the sample was decreased by e times in relation to I_0 was in the range of $(351-356)$ K.

Due to the fact that results shown in Fig. 2 could be affected by currents of pyroelectric nature and so-called thermostimulated currents [13], the response of sample $S2$ to the change in temperature was investigated without the use of external voltage source. In this case both electrodes on nonpolar faces were connected to the input resistor of

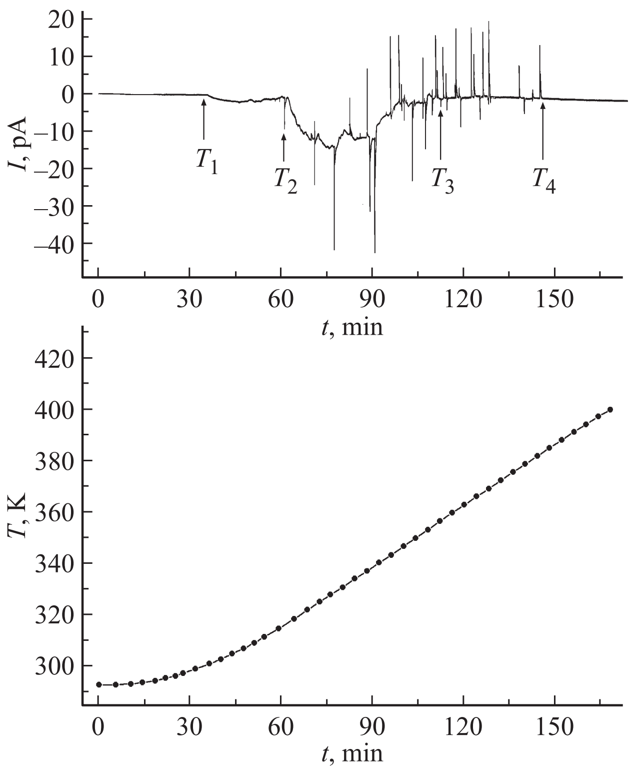

Figure 3. Response of sample $S2$ to heating in the mode of current generator.

the electrometric amplifier. Fig. 3 shows dependence of electrical response of sample S2 obtained in the process of its heating from room temperature.

A similar effect has been observed earlier in the investigation of the effect of temperature change on optical modulators made on plates of nonpolar cut of LN crystals [14]. The monotonous component of the current is most probably responsible for the drainage of excess charges from polar surfaces onto the measuring electrodes over the crystal surface, and the presence spikes (real amplitude can be as high as 4 nA) is explained by the capacitive response to the quick drop-off of both positive and negative excess screening charges from polar surfaces to the environment [14].

It is worth to note some typical points: $T_1 \cong 300\,\mathrm{K}$, $T_2 \cong 317\,\mathrm{K}$, $T_3 \cong 362\,\mathrm{K}$ and $T_4 \cong 383\,\mathrm{K}$. In the range from T_1 to T_2 probably a recombination of excess charges takes place inside the surface layer and their partial drainage onto measuring electrodes; in the range from T_2 to T_3 the drainage of excess screening charges onto electrodes is combined with their drop-off from the polar surfaces. In the range from 356 to 383 K mainly a drop-off of electrons and probably of H^+ ions is observed. At temperatures above 383 K pulse spikes disappear, which may be indicative of the self-compensation of excess charges due to the residual surface conductivity of the sample with the formation of neutral H^0 atoms. At the same time, according to the *ab initio* calculations of [15] the desorption of H_2O molecules on the $+z$ surface of LN takes place at a temperature of $T_{d1} = 325\,\mathrm{K}$, and desorption on the $-z$ surface takes place at $T_{d2} = 450\,\mathrm{K}$.

Fig. 4 shows time dependence of the electrical response of sample $S2$ obtained at the same connection in the cooling mode with varying temperature change rate V in the preselected temperature range.

It is clearly seen that at temperatures below $T_{\mathrm{ord}} \cong 405\,\mathrm{K}$ the electrical response has both a weak, slowly changing constant component and short pulses (with a real amplitude of about 20 pA), which density correlates with the value of V. There are no pulses at $T > T_{\mathrm{ord}}$.

Due to the fact that the temperature dependence of specific electric conductivity of sample $S2$ along the z axis $\sigma_z(T)$ is known [11], the time of so-called Maxwell relaxation can be calculated as $\tau = \rho_{33}(T)\varepsilon_{33}(T)\varepsilon_0$, where $\rho_{33}(T)$ being specific resistance along the polar axis of the sample, $\varepsilon_{33}(T)$ being correspondent component of the permitivity tensor at $T = 406\,\mathrm{K}$. Assuming that $\varepsilon_{33}(T)$ corresponds to the data of [9], we get $\tau\big|_{406\,\mathrm{K}} \cong 91$ sec. Thus, with cooling of sample S2 and $T < 406\,\mathrm{K}$ screening of the depolarizing field by internal mechanisms is possible only at sufficiently low rates of crystal temperature change. Hence, the cause of pulse spikes observed in Fig. 4 is the adsorption of H_2O molecules on the crystal surface and their dissociation, which probably takes place after accumulation of a certain quantity of H_2O on the surface. This is evidenced by equal amplitudes of the spikes.

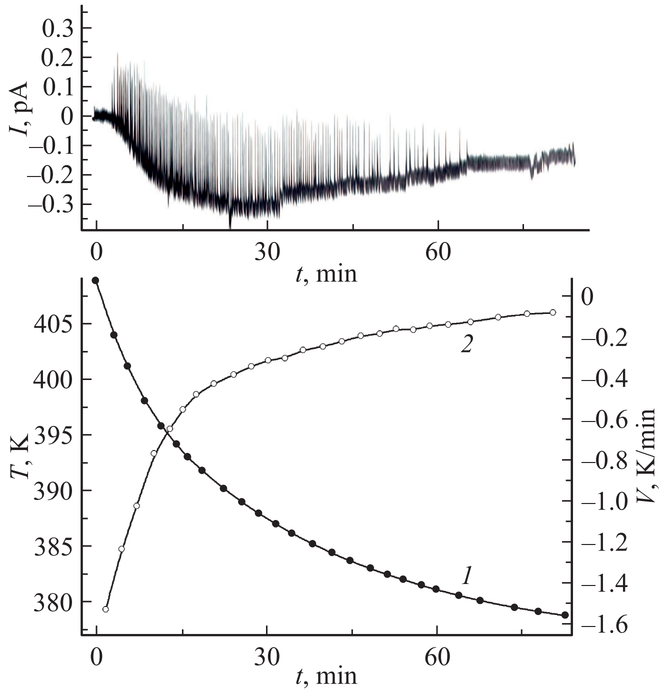

Figure 4. Response of sample $S2$ to cooling in the mode of current generator. (*1*) — time dependence of temperature; (*2*) — temperature change rate.

4. Discussion of results

It is in no doubt that the cause of the strong surface conductivity over the polar faces of LN crystals is the adsorption of H_2O molecules, because after the heating of samples at a temperature of $\sim 450\,K$ followed by their cooling to room temperature in the presence of dried silica gel resistance of samples $S1$ and $S3$ at $T = 300\,K$ increases by more than an order of magnitude, and that of sample $S2$ increases by approximately 10^7 times. Nonetheless, this circumstance does not make clear the causes of the extremely strong surface conductivity over polar surfaces of sample $S2$.

A very important characteristic of ferroelectric materials that has an effect on their physical properties [16] is the unipolarity of sample ξ, which is determined as follows:

$$\xi = \frac{V^+ - V^-}{V^+ + V^-},$$

where V^+ and V^- are total volume of positive and negative domains, respectively. At the same time, the real value of spontaneous polarization of the sample is $P = \xi P_0$, where P_0 being spontaneous polarization of the single-domain crystal.

Therefore, pyroelectric properties of all three samples were studied. The measurements were taken at $V \sim 0.1$ K/min. Taking into account corrections for thermal expansion of crystals, formula that establishes the relationship between the primary pyroelectric coefficient γ_1 and the current I through the load resistor is as follows [17]:

$$\gamma_1 = -\frac{dP(T)}{dT} = -\frac{I}{SV} + 2P(\alpha_a + \alpha_b) = \gamma' + 2P(\alpha_a + \alpha_b),$$

where $P(T)$ is spontaneous polarization of the crystal, S is area of polar faces, T is temperature, α_a and α_b are coefficients of linear temperature expansion along nonpolar axes a and b, γ' is uncorrected pyroelectric coefficient.

$\gamma'(T)$ dependencies for samples $S3$ and $S2$ are shown in Fig. 5 and results of experimental data approximation by a first-order polynomial $\gamma'(T) = a + bT$ are presented in Table 2.

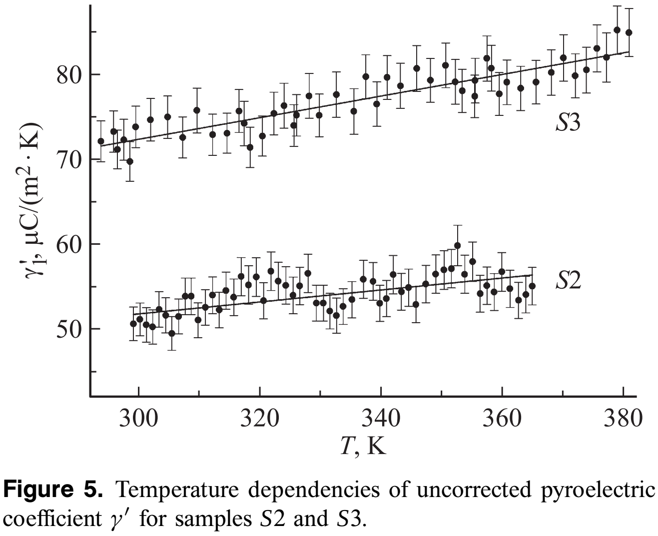

Figure 5. Temperature dependencies of uncorrected pyroelectric coefficient γ' for samples $S2$ and $S3$.

Table 2. Pyroelectric properties of studied crystals

Sample	γ' at 300 K, $\mu C/(m^2 \cdot K)$	a, $\mu C/(m^2 \cdot K)$	b, $\mu C/(m^2 \cdot K^2)$	ξ
$S1$	70 ± 3	35.1 ± 3.1	0.12 ± 0.02	~ 1
$S2$	50 ± 2	30.7 ± 3.7	0.07 ± 0.01	~ 0.69
$S3$	72 ± 3	34.2 ± 2.9	0.13 ± 0.01	~ 1

Sizes of the studied samples are rather close to each other, therefore the temperature gradient inside samples at the same heating rates will have the same effect on the experimental results for all studied samples. It can be seen from Table 2 that a and b parameters of the polynomial for sample $S2$ are considerably less than those of samples $S1$ and $S3$, and values of $\gamma'|_{300\,K}$ of $S1$ and $S3$ coincide to each other within the accuracy.

Taking into account that α_a and α_b of LN crystals with a congruent composition and of Mg-doped LN coincide with each other within the accuracy [18,19], and the $\gamma'(T)$ dependencies of samples $S1$ and $S3$ are also close to each other, it can be assumed as a first approximation that $P \sim \gamma'$. Then, assuming that samples $S1$ and $S3$ are almost single-domain, the unipolarity of sample $S2$ can be evaluated. This value is presented in Table 2 as well. Thus, it is supposed that sample $S2$ initially was just partially single-domain. It means that there is a large number of domain boundaries on polar surfaces. It is absolutely evident that without foreign screening charges in the region of domain boundaries the polar surfaces should have a strong inhomogeneous electric field. This field attracts polar H_2O molecules to the surface from the air and probably promotes their dissociation according to the scheme of $H_2O \rightarrow OH^- + H^+ \rightarrow 2H^+ + 2e^- + O^0$ with further capture of the formed H^+ ions and free electrons by the $-z$ and the $+z$ polar surfaces, respectively.

In favor of this hypothesis says the fact that at a quick heating of LN and LT crystals the change in the excess screening charge on the $+z$ surface is realized in the form of electron emission [20], which under certain conditions results in x-ray radiation [21].

5. Conclusion

Based on the above-presented experimental results the following conclusions can be made. In normal conditions partly dissociated H_2O molecules always present on the LN crystal surface, which results in the surface conductivity. At the same time, the probability of their adsorption probably depends on the unipolarity of the crystal. If this assumption is true, then a strong effect of the adsorbed water on the parameters of products based on the periodically polarized LN should be expected [22].

Conflict of interest

The author declares that he has no conflict of interest.

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