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# MODIFICATION OF THE ELECTRICAL PROPERTIES OF $LiNbO_3$ SINGLE CRYSTALS BY ANNEALING IN SATURATED WATER VAPOR

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Electrical and optical properties of the $LiNbO_3$ single crystals which were annealed in saturated $H_2O$ and $D_2O$ vapor were investigated. It is found that the activation energy of the electrical conductivity for these samples is close this value of LN samples, reduced in hydrogen atmosphere. It is shown too, that the annealing of $LiNbO_3$ in saturated $H_2O$ vapor also leads to a strong increasing of the optical absorption of the samples in visible area. The nature of this phenomenon is discussed.
***Keywords:*** $LiNbO_3$, annealing, electrical conductivity.

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## INTRODUCTION

Ferroelectric lithium niobate (LN) $LiNbO_3$ is technologically important material with wide applications in nonlinear optics and electro-acoustic devices. It is well-known that the high temperature annealing in reducing environments containing hydrogen strongly influenced the electrical and optical properties of LN crystals [1-6]. It is established, that heating LN wafers in benzoic acid vapor causes formation of protons enriched surface layers with few μm thickness in them [4]. At the same time the investigation of interrelated changes of the electrical properties and IR optical spectra for LN treated in $H_2O$ vapor or $H_2$, do not provide definitive answers on the entry of $H^+$ into LN structure. For example in [2, 3] was not observed any changes of electrical and optical properties of LN annealed in $H_2O$ vapor flow.

On the other hand, changes of electrical properties and increasing of absorption in $OH^-$ and $OD^-$ bands after annealing in ampoules with $H_2O$ vapor at $P = 10…30$ bar were observed in [2, 3] earlier. But comparison of the changes of LN electrical properties their optical properties in visible and IR range after annealing in $H_2O$, $D_2O$ vapor and $H_2$ atmosphere is not performed in a single study. The aim of the present paper is to obtain the additional information through the investigation of electrical and optical properties of LN crystals, annealed in $H_2$, $H_2O$ and $D_2O$ saturated vapor.

## 1. EXPERIMENTAL DETAILS

For our experiments we use the samples which were cut from the same boules of congruent LN grown at SRC "Carat" [7]. Samples №1 and №2 were annealed at 600 ºC for 1 h in the $H_2$ atmosphere in separate ampoules. Sample №3 was annealed at 500ºC for

5 h in saturated $H_2O$ vapor and samples №4-5 were annealed at 500ºC for 5 h in saturated $D_2O$ vapor. All samples were carefully polished to obtain a good optical quality. Annealing was held in ampoules at a pressure $P \approx 1$ bar.

The measuring of the optical absorption coefficient α in a visible part of spectra were realized at room temperature for three fixed wavelength (λ=625, 525 and 465 nm) when the wave vector **k** is coincide to the polar axis **z** of a crystal by using a simple home-made device. Optical absorption coefficient were calculate according to Beer-Lambert law: $\alpha = d^{-1} \cdot \ln(I_o/I)$, where $I_0$ and $I$ are the intensity of incident light and transmitted light and $d$ is a sample thickness.

Electrical properties of the samples were studied with a specially designed device, which can realize the measurements of electric impedance (frequency range $10^{-3}\ldots10^{5}$ Hz) and dc conductivity of the crystals [8].

## 2. RESULTS AND DISCUSSION

First of all the measurements of optical absorption of all annealed samples were realized and these data are presented in the Table. Optical measurements revealed no significant differences in the values of the absorption coefficients of the crystals which were annealed in saturated $H_2O$ and $D_2O$ vapor. Moreover the obtained values of optical absorption for the crystals, treated in pure hydrogen and in $H_2O$ (or $D_2O$) vapor are perfectly comparable – taking into account the difference of treatment temperature.

Table 1

Optical absorption coefficients and activation energy of electric conductivity for all annealed samples

| sample | $\alpha_{625\ нм}$, cm$^{-1}$ | $\alpha_{525\ нм}$, cm$^{-1}$ | $\alpha_{465\ нм}$, cm$^{-1}$ | $E_a$, eV |
|---|---|---|---|---|
| №1 | 5.6 ± 0.1 | 5.8 ± 0.1 | 5.8 ± 0.1 | 0.67 ± 0.01 |
| №2 | 5.9 ± 0.1 | 6.3 ± 0.1 | 6.5 ± 0.1 | 0.68 ± 0.01 |
| №3 | 1.55 ± 0.05 | 1.82 ± 0.05 | 1.95 ± 0.05 | 0.70 ± 0.01 |
| №4 | 1.91 ± 0.05 | 2.30 ± 0.05 | 2.42 ± 0.05 | 0.70 ± 0.01 |
| №5 | 2,26± 0.05 | 2,68± 0.05 | 2,68± 0.05 | 0.70 ± 0.01 |

Temperature dependences of the specific electrical conductivity (σ) of three investigated samples along $z$ axis in a temperature range 294…370 K obtained by two-terminal method and usual dc technique are presented in Fig. 1. They are fully described by simple Arrhenius law with the similar activation energy $E_a$ (indicates in a Table 1). Additional experiments were preformed using three-terminal method for excluding the surface conductivity and these results are in good agreement with those, shown in Fig. 1.

These results are unexpected, because predicted increasing of $OH^-$ or $OD^-$ groups volume concentration in the annealed samples must lead to the increasing of the ionic contribution to electrical conductivity of the samples and the respective activation energy must be equal to 1,00…1.12 eV. [1, 6]. Increasing of $OH^-$ volume concentration in the crystal can not strongly affect its electrical conductivity at room temperature. But specific electrical conductivity of non-annealed LN crystals at room temperature is equal to $(10^{-15}\ldots10^{-16})$ $(\Omega\cdot cm)^{-1}$ and this value is by some orders smaller that for reduced LN crystals. Moreover, in accordance with the data obtained earlier [9] conductivity of LN annealed in $H_2O$ vapor flow is close to the value for non-annealed sample.

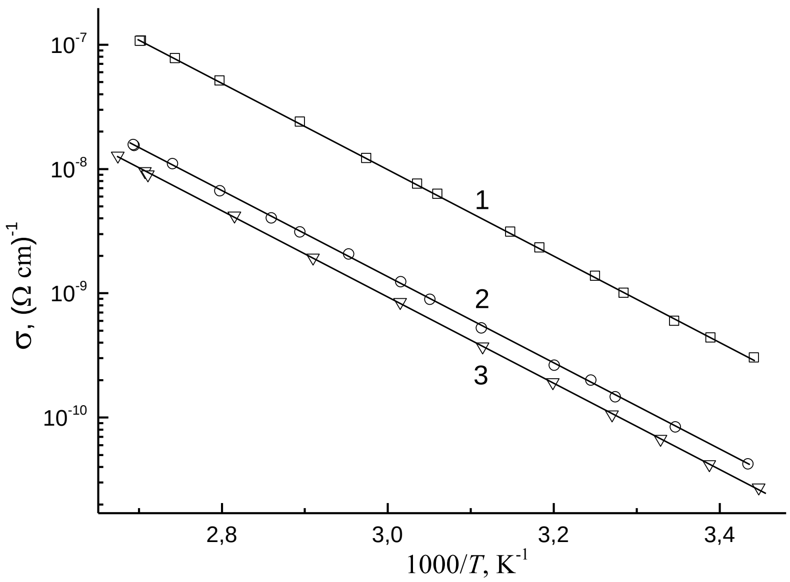


Fig. 1. Temperature dependence of the specific electric conductivity of annealed LN samples: (1) – sample №2; (2) – sample №3; (3) – sample №4.

Measuring the electrical conductivity of the sample №4 showed the presence of small quantities of conductivity anisotropy along the polar and non-polar axis (as in the case of the sample annealed in a hydrogen atmosphere). Since all investigated samples, annealed in ampoules are characterized by the similar value of activation energy, one can conclude that the nature of the main contribution to their electrical conductivity is identical.

It was demonstrates earlier [10] that non-controlled heating of LN samples, which were early reduced in hydrogen, up to 430...450 K leads to significant decreasing of sample electric conductivity along polar axis (more then twice at $T = 300$ K). This effect was explained as a result of the possible diffusion of atmospheric oxygen into a near-surface layers of reduced sample. It may lead to the destruction of bipolarons in these layers and a sharp increasing of these layers resistance.

For the testing of this assumption we investigate the temperature dependence of electrical conductivity of the sample №4 by impedance spectroscopy - before and after additional heat treatment in dry air at 573 K during 3 h. It is estimated that Nyquist diagrams of the sample №4 before additional heat treatment can be described by practically ideal semicircle in a temperature range (300...390) K. It is a serious argument to believe the uniformity of electric properties of the sample.

In accordance to our prediction, the additional heat treatment in dry air at 573 K strongly influenced the electrical properties of LN sample №4. Typical Nyquist diagram obtained in this series of experiments is shown in Fig. 2. Nevertheless, the optical absorption coefficient after additional heating was not change in the limits of experimental errors.

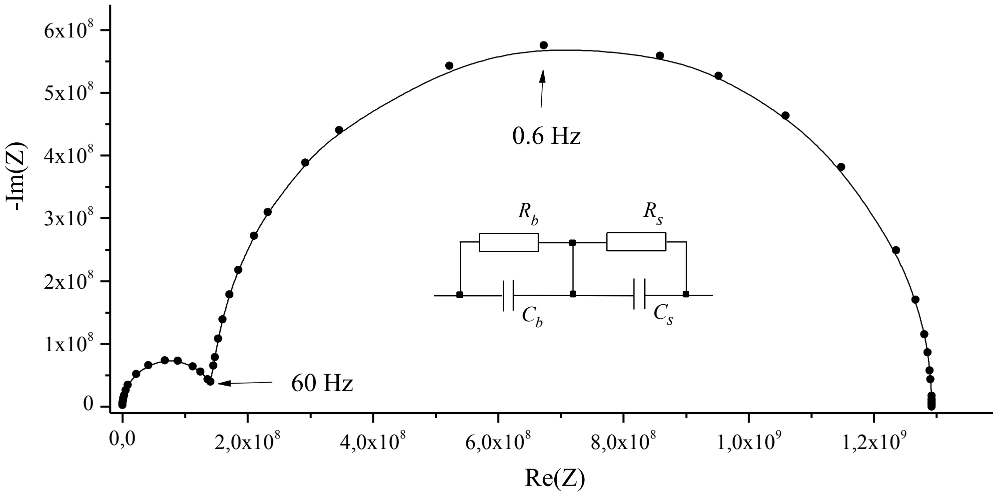


Fig. 2. Nyquist diagram of the sample №4 after additional heating in dry air, obtained at $T = 356$ K. Equivalent electrical circuit of the sample is shown in inset.

The data which are illustrate by Fig. 2 demonstrates that equivalent electrical circuit of the crystal can be presented as a consecutive connection of two parallel *RC* chains, one of which simulate the crystal's internal volume and described by capacity $C_b$ and resistance $R_b$ and the second one simulate the capacity $C_s$ and resistance $R_s$ of near-surface layers. Respective circuit is shown in the inset of Fig. 2.

Due to analysis of impedance spectra according to this simple model, we determined the temperature dependences of electric conductivities $S_b$ and $S_s$ in the temperature range (300...450) K. These data illustrates by Fig. 3. It is concluded too, that the ratio of capacities $C_s/C_b$ is temperature independent in a limits of experimental errors and is equal to (50 ± 7).

In a process of investigation of LN crystals reduced in hydrogen it was estimate, that this annealing do not affects the components of the tensor of dielectric permittivity $\varepsilon_{11}$ and $\varepsilon_{33}$ in analyzed here temperature range [10]. So we can try to evaluate the depth of the near-surface layers in which diffusion of atmospheric oxygen results in a destroying of the majority of bipolarons, which are responsible for the electric conductivity of "black" LN crystals.

According to the equivalent circuit of the crystal, which is illustrates by Fig. 2, the total depth of electrically modified near-surface layers ($d_l$) approximately will be equal to

$$d_l \cong \frac{C_s}{C_s + C_b} d_c$$

where $d_c$ is a thickness of the crystal. In a result we obtain that $d_l$ = (69 ± 7) μm. It is clear that the varying of additional heat treatment conditions gives a possibility to investigate the dynamics of the oxygen diffusion into a "black" LN crystal.

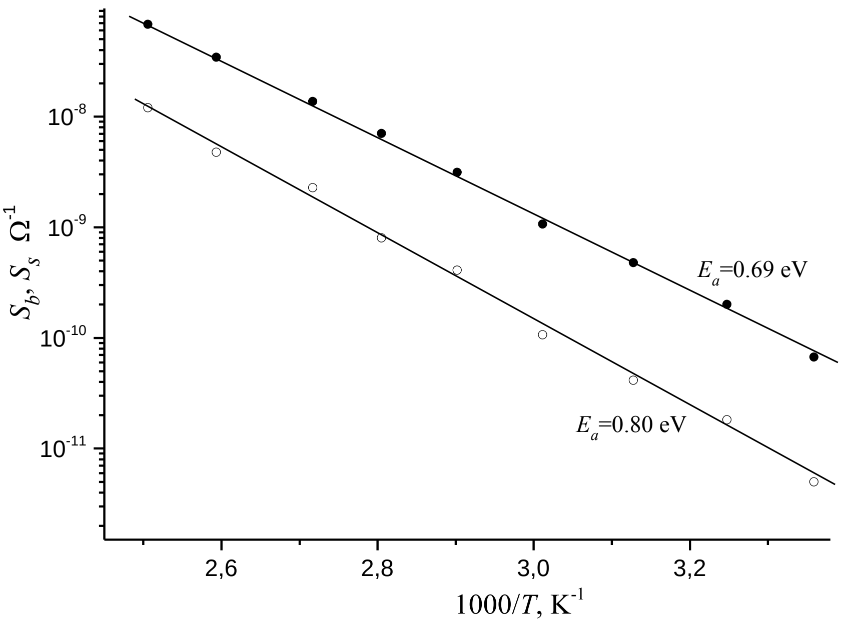


Fig. 3. Temperature dependences of $S_b$ (open circles) and $S_s$ (dash circles) for the sample №4 after additional heating in dry air. Mean values of activation energy are pointed too.

**CONCLUSIONS**

So the annealing of LN crystals in saturated $H_2O$ or $D_2O$ vapor (at negligible oxygen partial pressure) and a pure $H_2$ probably affects the electrical properties by the same way. The annealing in these media leads to the oxygen loss in the crystal and forming of oxygen vacancies and bipolarons.

Taking into account the data obtained by us, we can conclude that the annealing of congruently grown LN crystals in saturated pure $H_2O$ or $D_2O$ vapor in ampoules at 500 °C and $P \approx 1$ bar leads to changes of LN optical properties in visible range as well as electrophysical properties similar as those that occur after reducing treatment in $H_2$ atmosphere. Thus it can be assumed that the main reason for the increasing of the LN conductivity after annealing in ampoules with $H_2O$ or $D_2O$ is formed bipolarons.

It has been established, that the additional heat treatment in dry air of the "black" LN samples leads to the electric modification of its near-surface layers. Investigations of the oxygen diffusion, which is responsible to this phenomenon, will be the goal of the next experiments.

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**Притуленко А. С. Модифікація електричних властивостей монокристалів $LiNbO_3$ відпалюванням у насиченій водній парі / А. С. Притуленко, О. В. Яценко, Д. Ю. Сугак, В. М. Сольский //** Вчені записки Таврійського національного університету імені В. І. Вернадського. Серія : Фізико-математичні науки. – 2014. – Т. 27 (66), № 2. – С. 79-85.

Досліджено електричні та оптичні властивості монокристалів $LiNbO_3$, що пройшли відпалювання у насиченій парі $H_2O$ та $D_2O$. Встановлено, що енергія активації електричної провідності в таких зразках є близькою до значення, що спостерігається для зразків НЛ, що пройшли відпалювання у водні. Також встановлено, що відпалювання у насиченій водяній парі призводить до сильного збільшення оптичної густини зразка у видимій області. Обговорюється природа цих ефектів.

***Ключові слова:*** $LiNbO_3$, ,відпалювання,, електричні властивості.

**Притуленко А. С. Модификация электрических свойств монокристаллов LiNbO3 отжигом в насыщенных парах воды / А. С. Притуленко, А. В. Яценко, Д. Ю. Сугак, И. М. Сольский //** Ученые записки Таврического национального университета имени В. И. Вернадского. Серия : Физико-математические науки. – 2014. – Т. 27 (66), № 2. – С. 79-85.

Исследованы электрические и оптические свойства монокристаллов $LiNbO_3$, прошедших отжиг в насыщенных парах $H_2O$ и $D_2O$. Обнаружено, что энергия активации электрической проводимости в таких образцах близка к значению, наблюдаемому для образцов НЛ, восстановленных в водороде. Также обнаружено, что отжиг в насыщенных парах воды приводит к сильному увеличению оптической плотности образца в видимой области. Обсуждается природа этих эффектов.

***Ключевые слова:*** $LiNbO_3$, отжиг, электрические свойства.

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