

Modification of Electric Properties of Lithium Niobate Crystals by Ion Bombardment

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Abstract – The effect of the insulator-conductor transition of surface layers of oxides by ion bombardment was investigated by the example of doped LiNbO_3 single crystals. The aim of this work is investigation the influence of impurity MgO , and also impurity of Fe_2O_3 on efficiency of conducting layers formation in LN crystals by ion bombardment. The important role of reduction in modification of conducting properties of the ion-irradiated crystals was established. The action of reduction on the electric characteristics of crystals LiNbO_3 is similar to that of ion bombardment. A new band of optical absorption with a maximum at 3.7 eV caused by presence of Mg impurity in $\text{LiNbO}_3 + \text{MgO}$ was founded. Threshold effect of MgO doping in LiNbO_3 sample is observed around 10 mole% of MgO in LiNbO_3 host and the origin of threshold effect is the formation of (Mg_{Nb}) defects. The comparative analysis of electric properties of reduced and irradiated by Ar^+ ions crystals shows, that conductivity of the lithium niobate ion-modified layers is carried out by polarons hopping.

1. Introduction

Lithium niobate LiNbO_3 (LN) is a very perspective material for creation of devices of processing and transfer of the information. In this connection, its properties are studying intensively [1–4]. During researches the opportunity of optical and electric properties regulation of LN by heat treatment in oxidation-reduction conditions was established, and also the essential influence of heat treatment in reducing conditions on conductivity of crystals is shown.

Ion irradiation of insulators transfers their surface in a state with high electric conductivity $\sigma_s > 10^{-4} - 10^{-6} \Omega^{-1}$ and low activation energy about (0.01–0.002) eV. The role of violation of crystals stoichiometry under action of ion irradiation is very important in this phenomenon. Lithium niobate crystals (LN) very easy change their stoichiometry by doping or thermal treatment and this capability was used for understanding the nature of ion-induced conductivity of oxygen-containing insulating crystals.

The significant number of works was devoted to research of influence of impurity on various properties of crystals LN, thus the special role Mg was found out. It is revealed, that there is a critical concentration

of impurity $[\text{Mg}]_C$ about 5–6 mol% when physical properties of lithium niobate significantly change.

Iron as impurity usually, occupies in a lattice of LN regular lithium position, forming defects of replacement Fe_{Li} . A charge state is either Fe^{2+} or Fe^{3+} . Fe^{3+} is characterized by optical absorption at 1.1 eV and about 2.6 eV. Reduction is accompanied by re-charge $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$. At an annealing temperature 720 K iron ions completely change its valence [3]. All the investigation carried out until now demonstrate significant violation of crystal stoichiometry and influence of this phenomenon on a wide complex of their physicochemical properties.

Therefore it is interesting to investigate the influence of impurity MgO , varying in limits of (0–10) mol % and also impurity of Fe_2O_3 on efficiency of conducting layers formation in LN crystals by ion bombardment.

Single crystals were grown by the Czochralski method from congruent melt. Crystals were cut on *c*-oriented plates of 1 mm thickness, and then were polished. Crystals were irradiated by argon ions Ar^+ with energy 150 keV and fluence 10^{16} ions/cm². The choice of ions Ar^+ is caused by desire to exclude influence of implanted impurity nature on conductivity of crystals and emphasized thus influence of defects of radiating origin.

2. Experiment and Discussion

The method of investigation included a series of oxidation-reduction annealing of samples before and after ion irradiation and subsequent measurement bulk (σ_v) and surface (σ_s) conductivity. Oxidation of crystals took place in air; reduction was carried out in vacuum 10^{-5} and 10^{-2} Torr.

Previously performed analysis [5] has shown that from possible mechanisms of charge transfer (ionic, electrons in conducting band, hopping of electrons) at low temperatures the most preferable is the electrons hopping. It is supposed, that the hops of electrons are carried out between localized states created by antisite defects in different states.

The received results in a complex with the data of optical measurements testify also that doping of LN crystals by magnesium results in decrease of density of antisite defects that entail the change of the parameters of conductivity, connected with these states.

Doping of MLN crystals by iron impurity in different concentration ($\text{LiNbO}_3 + 5.0 \text{ mol\% MgO} + 100 \text{ ppm Fe}_2\text{O}_3$; $\text{LiNbO}_3 + 5.0 \text{ mol\% MgO} + 300 \text{ ppm Fe}_2\text{O}_3$; $\text{LiNbO}_3 + 5.0 \text{ mol\% MgO} + 600 \text{ ppm Fe}_2\text{O}_3$ (FMLN)) results in appearance of optical absorption connected to presence of the ions Fe^{2+} and Fe^{3+} . The absorption band with maximum at 2.58 eV, appropriate to ionization of ions Fe^{2+} with electron transition to conductive band [2].

Ion irradiation of FMLN samples, as well as MLN samples results in appearance of unstructured additional absorption at the edge of own optical absorption. However in contrast of MLN crystals the edge of this additional absorption induced by ion irradiation is displaced not in region of short wavelength, but to the realm of the large wavelength with growth of iron impurity concentration. Doping of iron impurity in various concentrations in addition to MgO impurity does not render in principle influence on efficiency of ion-thermic formation of a conducting state of crystals LiNbO_3 .

The results of ion-modified layers conductivity measurement are represented in Fig. 1 and demonstrate that joint influence of impurity MgO and Fe_2O_3 is identical to influence of magnesium impurity.

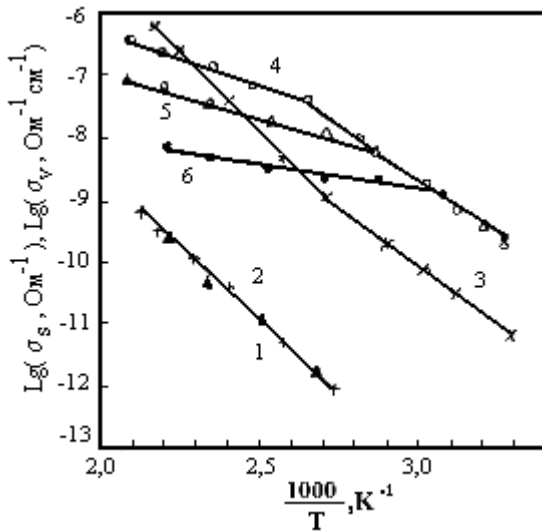


Fig. 1. Conductivity of ion-modified layers of lithium niobate versus reciprocal temperature. Sample 5FMLN-300. Ar^+ , $10^{16} \text{ ions/cm}^2$: 1, 2 – σ_v and σ_s before irradiation; 3 – σ_s as-irradiated; 4, 5, 6 – σ_s after successive reduction at 600 K

It is connected first of all with similarity of behavior of iron ions in a lattice of LiNbO_3 and that of magnesium ion [2]. Both, first and second are arranged in Li vacancies, competing not only with niobium ions, but also among themselves. The joint action of 5 mol% of MgO and Fe_2O_3 with concentration less than 600 ppm is similar to the action of MgO with concentration $[\text{Mg}] > [\text{Mg}]_c$.

The introduction of Fe_2O_3 impurity in concentration 600 ppm displaces the electrical characteristics of FMLN ion-modified layers to properties characteristic

for LiNbO_3 congruent crystals. It is clear from analysis of the data on conductivity of crystals of different chemical compositions. Foregoing proves to be true by the data of measurements of optical absorption spectra of FMLN samples.

Thus, the behavior of the ion-modified layers of crystals LiNbO_3 with both MgO and Fe_2O_3 impurities is a joint action and competition of magnesium and iron ions.

The significant interest for understanding mechanism of conductivity of ion-irradiated layers has information concerning temperature stability generated by ion irradiation states relative oxidizing annealing. Reduction radically changes the state of a surface of crystals of all investigated structures, resulting in significant growth of conductivity of samples (more than 5 orders and reaching the magnitude 10^{-8} – $10^{-11} \Omega^{-1}$ at room temperature). The results show that action of reduction on conductivity in many respects similarly to action of ion irradiation. The summary results given in Fig. 2 show that for the majority of compositions of crystals the surface conductivity is multistage and has exponential character.

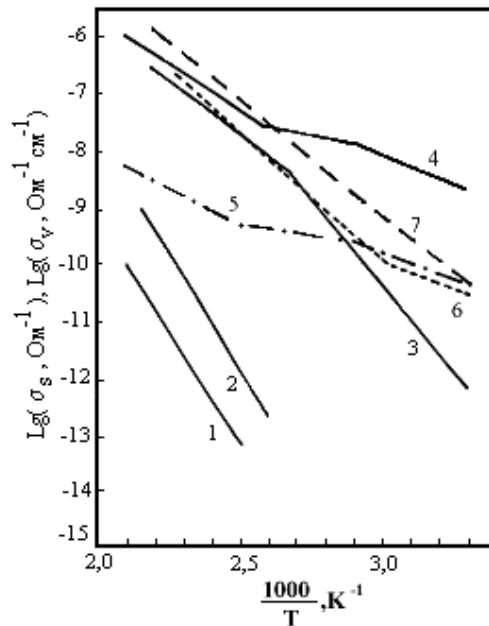


Fig. 2. Surface conductivity σ_s MLN crystals reduced at $T = 870 \text{ K}$. 1, 2 – σ_v and σ_s before reduction; 3 – MLN-0; 4 – MLN-2.5; 5 – MLN-5.0; 6 – MLN-6.0; 7 – MLN-10.0

The effect of increase of conductivity as a result of reduction depends on MgO concentration.

This effect is maximal for pure LN and decreases with growth of MgO contents. It takes place both for surface (σ_s) and bulk (σ_v) conductivity. Activation energy of conductivity (both σ_s and σ_v) is increased with growth of MgO concentration. Comparison with similar dependencies for the LiNbO_3 crystals irradiated by Ar^+ ions ($\Phi = 10^{16} \text{ ions/cm}^2$) shows similarity in behavior, of conductivity and activation energy E for reduced and irradiated samples.

Reduction essentially modifies electronic spectrum of LiNbO₃ crystals and this manifests in character of conductivity temperature dependence. As it is possible to see in Fig. 2, there are 3 stages on temperature dependence of conductivity, which is characterized by different activation energy. The existence of three stages in temperature dependencies of conductivity with different values of activation energy demonstrates existence of three mechanisms of conductivity, which are caused by peculiarities of LiNbO₃ electron spectrum. The received experimental results and literary data do not allow to define exactly the mechanism of conductivity at each stage. It is possible to make some assumptions concerning the mechanism of conductivity. The conductivity of reduced LiNbO₃ crystals has character of charge carriers hopping at temperature $T > 300\text{K}$. Thus it is possible that the first stage in temperature dependence of conductivity is connected with electrons transition from band of defects to the localized states with energy nearby level of percolation. In this case activation energy of conductivity $U = E_F + \Delta E$, where E_F is Fermi level and ΔE is activation energy of hopping over localized states.

Increase of temperature results in an exhaustion of band of defects, and this manifest itself in change slope of temperature dependence of $\lg \sigma_s = f(1/T)$. The activation energy in this case $U = \Delta E$, that is smaller than at the first stage. This is observed experimentally. The further increase of temperature results in change of slope of conductivity temperature dependence at the temperature T about 400K. Polarons effects are quite possible to observe in this region of temperatures and activation energy grows in comparison with the second stage. Then the activation energy should consist of activation energy of polarons hopping $E_p = \frac{E_p}{2} \approx (0.35 - 0.4) \text{ eV}$ [4], where $E_p = 0.8 \text{ eV}$ is the energy of polarons bond.

Thus, the conductivity of ion-irradiated layer of LN and MLN crystals has electronic character. The basic mechanism of charge transfer in LiNbO₃ crystals with $[\text{Mg}] < [\text{Mg}]_C$ is the hopping of charge carriers on the located states. In crystals with $[\text{Mg}] > [\text{Mg}]_C$ the conductivity is connected probably with carriers exited in nonlocalized states.

Taking into account, that the Fermi level in LN lays below bottom of conduction band on $\sim 0.26 \text{ eV}$ we shall receive activation energy at the third stage $E = (0.6 - 0.7) \text{ eV}$ and this observed experimentally.

Thus, the received results show that:

Reduction of LiNbO₃ crystals pure, and also with different contents Mg results in increase of their conductivity ($10^5 - 10^8$) times. The value of σ_s depends on the contents of Mg impurity in crystals. With growth of concentration [Mg] the efficiency of creations of a conducting states decreases. The action of reduction on the electric characteristics of crystals LiNbO₃ is similar to that of ion bombardment.

The value of σ_s depends on the contents of Mg impurity in crystals. The efficiency of conductive state creation decreases with growth of [Mg] concentration.

The temperature dependence conductivity is multi-stage and also described by exponential function.

There is a system of localized states in initial crystals of lithium niobate because of non-stoichiometry and charge transfer occurs by hopping of carriers over its.

The analysis of probable mechanisms of charge transfer (ionic, electronic by conductive band electrons, electronic by electron hops) in LiNbO₃ crystals has shown that in the low-temperature region electrons hopping is the most preferable. Thus it is supposed, that the hops of electron are carried out between localized states formed by antisite defects, situated in different energetic states. Doping the LiNbO₃ crystals by Mg²⁺ ions leads to decrease of antisite defects density and results in change of the parameters of charge transfer.

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