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## THE COMBINED ELLIPSOMETRIC METHOD OF COMPLETE OPTICAL CHARACTERIZATION OF CRYSTALS IV. APPLICATION TO UNIAXIAL CRYSTAL

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In the fourth part of the article, the application of the proposed method for the complete optical characterization of crystals to optically uniaxial crystals is considered. The object of the study was lithium niobate ( $\text{LiNbO}_3$ ) crystals. Refining the orientation of the optical indicatrix in the samples under study, we confirmed the conclusion by direct measurements that for the implementation of the proposed combined ellipsometric method, knowledge of the crystallographic orientation of the crystal under study is completely optional. The obtained values of the optical constants of the undoped  $\text{LiNbO}_3$  crystal [ $n_o = 2.280(\pm 0.003)$ ,  $n_e = 2.202(\pm 0.002)$ ,  $\Delta n = -0.0775(\pm 0.0015)$ ] fully confirmed the correctness of the proposed method and its efficiency in the investigation of uniaxial crystals. The sensitivity of the combined ellipsometric method was tested on  $\text{LiNbO}_3$  crystals subjected to high-temperature annealing in an  $\text{H}_2\text{O}$  atmosphere. The optical constants obtained for an undoped  $\text{LiNbO}_3$  crystal [ $n_o = 2.2455(\pm 0.0015)$ ,  $n_e = 2.1965(\pm 0.0015)$ ,  $\Delta n = -0.049(\pm 0.001)$ ] and a magnesium-doped  $\text{LiNbO}_3$  crystal [ $n_o = 2.2445(\pm 0.0015)$ ,  $n_e = 2.1756(\pm 0.0007)$ ,  $\Delta n = -0.069(\pm 0.001)$ ] is significantly less than the optical constants of the as grown crystal. It is assumed that the main reason that caused such significant changes is high-temperature annealing in an  $\text{H}_2\text{O}$  atmosphere. Our main goal was to show the applicability of the method to the analysis of possible changes in the optical constants of a crystal caused by the influence of various factors on its properties. The results obtained show that the goal has been achieved.

*Key words:* ellipsometry, optical indicatrix, principal refractive indexes, uniaxial crystals, lithium niobate

### 1. Introduction

In the three previous parts of this article [1-3], all stages of the combined ellipsometric method for the complete optical characterization of crystals were described in detail. In this part of the article, we will consider the application of this method to the characterization of optically uniaxial crystals. Lithium niobate crystals ( $\text{LiNbO}_3$ ) became the object of research. This choice is certainly not accidental. Due to their unique physical properties (high radiation resistance, high nonlinear optical, electro-optical, photovoltaic, pyroelectric, piezoelectric coefficients), lithium niobate crystals have found very wide application. In particular, lithium nio-

bate is used in optical radiation generators, optical modulators, memory elements, frequency converters, deflectors, and various telecommunication devices [4–11]. An intensive study of the  $\text{LiNbO}_3$  crystal began almost immediately after the discovery of the phenomenon of photorefractive in it [12]. Since that time, a huge number of articles devoted to the study of certain properties of lithium niobate have been published. The main results of these studies are quite fully summarized in several monographs and review articles [13–19]. It is clear that the optical properties of the  $\text{LiNbO}_3$  crystal have also been thoroughly studied (see, for example, [20–29]). Thus, we had a good opportunity to compare our results with those obtained by other researchers using other methods. In the second part of the article [2], we have already tested the proposed ellipsometric method on one of the  $\text{LiNbO}_3$  crystals. It was an undoped  $\text{LiNbO}_3$  crystal, the results of which fully confirmed the correctness of the method and the efficiency of its application for the optical characterization of crystals. However, it was necessary to expand the spectrum of the studied  $\text{LiNbO}_3$  crystals in order to more fully test the proposed method. In particular, we wanted to investigate a  $\text{LiNbO}_3$  crystal doped with magnesium oxide ( $\text{MgO}$ ). It is well known that the phenomenon of photorefractive, which is observed in an undoped  $\text{LiNbO}_3$  crystal [12], significantly limits its application in high-power laser radiation control devices [12, 19, 30 and 31]. Doping of lithium niobate with magnesium oxide eliminates the photorefractive properties of  $\text{LiNbO}_3$  and significantly increases its radiation resistance [32, 33]. Therefore, it was important to test our method specifically on  $\text{MgO}$ -doped  $\text{LiNbO}_3$  crystals. In addition, we had the opportunity to study  $\text{LiNbO}_3$  crystals subjected to high-temperature annealing. As is known, various atmospheres are used for the reduction annealing of  $\text{LiNbO}_3$  crystals: pure hydrogen [34, 35], argon [36, 37], various gas mixtures, for example, 90%  $\text{N}_2$  and 10%  $\text{H}_2$  [38], 95%  $\text{Ar}$  and 5%  $\text{H}_2$  [39] and annealing in vacuum [33, 40 and 41]. Therefore, we hoped that in this case it would be possible to compare the results obtained. In this work, we studied  $\text{LiNbO}_3$  crystals subjected to high-temperature annealing in an  $\text{H}_2\text{O}$  atmosphere. It should immediately be emphasized that our main goal was to test the applicability of our method to assess the effect of doping or annealing on the main optical parameters of the  $\text{LiNbO}_3$  crystal. We do not consider here the possible physical mechanisms that caused one or another change in the optical parameters of the crystal under study (especially since this cannot be done within the framework of ellipsometry alone). We only record these changes and compare them with the results of other researchers.

## 2. Brief description of the studied crystals of lithium niobate

This part of the article presents the results of studies of  $\text{LiNbO}_3$  crystals grown at the Scientific Research Company “Carat” (Lviv, Ukraine). The technology of growing just these crystals is quite fully described in [42–44]. Therefore, without going into details, we give for convenience only a brief description of the  $\text{LiNbO}_3$  crystalline samples studied by us. The crystals were grown from high quality raw materials by the Czochralski method. The initial raw material had a stoichiometric composition. In particular, the composition of the initial mixture was determined by flame photometry (lithium content) and gravimetric method (niobium content). The analysis showed that in the feedstock, the lithium content was in the range of 4.36–4.56 wt.%, and the niobium content was in the range of 62.9–63.5 wt.%. Such values are considered to correspond to the stoichiometric composition of  $\text{LiNbO}_3$ . To obtain a congruent ratio of components in the melt ( $R=\text{Li}_2\text{O}/\text{Nb}_2\text{O}_3=0.96$ ), a double recrystallization of the charge was carried out. This operation also made it possible to reduce the content of uncontrolled impurities in the feedstock to a level of  $<10^{-4}$  wt. % [42].

It is known [32, 33] that the effect of magnesium oxide on the properties of  $\text{LiNbO}_3$  crystals has a threshold character. The change in the properties of  $\text{LiNbO}_3$  occurs at MgO concentrations in the range of 5-7 mol.%. The specific value of the MgO concentration depends on the Li/Nb ratio in the grown crystal. In our case, when growing a  $\text{LiNbO}_3$ :Mg crystal, a mixture of stoichiometric composition was used, in which 19.7 g of MgO was added per 1 kg of mass, which corresponds to approximately 7 mol.% MgO in the crystal. As is well known [19],  $\text{LiNbO}_3$  single crystals after growth are polydomain. Therefore, immediately after the growth of the  $\text{LiNbO}_3$  crystal, the procedure of monodomainization is carried out. Monodomainization is performed in such a way that the domain polarization direction coincides with the crystal growth axis. In our case, monodomainization was performed in an AS-30 annealing furnace according to a special technique described in detail in [42]. Figure 1 shows the  $\text{LiNbO}_3$  crystals studied by us. During the preparation of the samples, their crystallographic orientation was preliminarily determined by the conoscopic method. After that, the samples were given the shape of a parallelepiped, the faces of which corresponded to the main planes of the crystal: (100), (010), (001). Therefore, to determine the optical constants of the crystal ( $n_o$ ,  $n_e$ ,  $\Delta n$ ), it was necessary to perform measurements on one of the planes: (100) or (010) [2]. All measurements were performed on a LEF-3M-1 laser ellipsometer ( $\lambda=632.8$  nm) at room temperature.

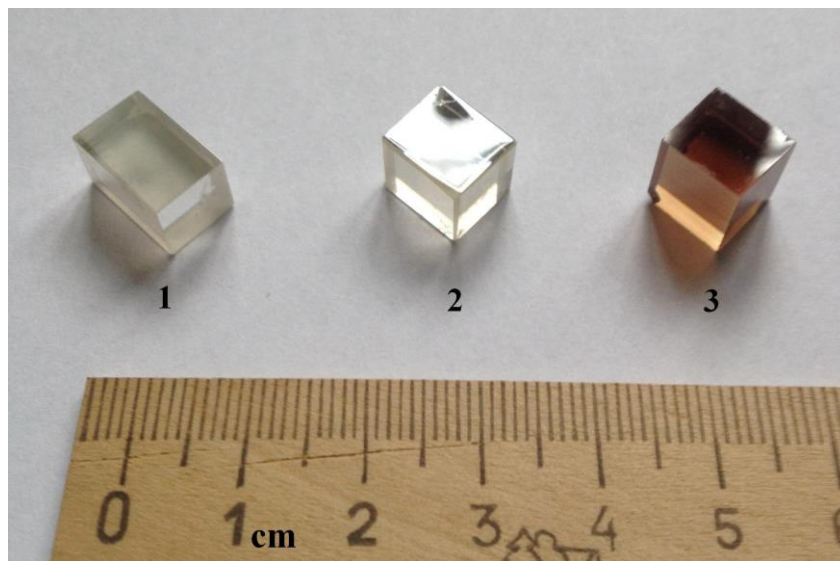


Fig.1.  $\text{LiNbO}_3$  crystals investigated in this work:

1 – undoped  $\text{LiNbO}_3$  crystal (sample LN-P1), 2 – undoped  $\text{LiNbO}_3$  crystal (sample LN-P2) annealed in  $\text{H}_2\text{O}$  atmosphere (temperature  $800^\circ\text{C}$ , pressure 10 bar, duration 5 hours), 3 – doped crystal  $\text{LiNbO}_3$  (+7 mol.% MgO) (sample LN-DM5) annealed in an  $\text{H}_2\text{O}$  atmosphere (temperature  $750^\circ\text{C}$ , pressure 10 bar, duration 2.5 hours).

### 3. Results of ellipsometric measurements of LiNbO<sub>3</sub> crystals and their analysis

Using our combined method for the complete optical characterization of crystals, at the first stage we refined the orientation of the optical indicatrix in the samples under study. Recall that in a LiNbO<sub>3</sub> crystal, the optical axis (and this is the crystallographic axis  $c$ ) is the only main axis of the optical indicatrix. Checking the orientation of the optical indicatrix in samples LN-P1 and LN-DM5 showed that the direction of the optical axis almost perfectly coincided with the predefined direction of the crystallographic axis  $c$ . The significant deviation was found in sample LN-P2. In particular, when measuring sample LN-P2 on the (100) plane (and this is the so-called  $X$  cut), we found that the main axis of the optical indicatrix is rotated by approximately  $14^\circ$  relative to the assumed direction of the  $c$  axis. Thus, if we take the results of measurements by our method as a basis, then it should be recognized that the crystallographic orientation of sample LN-P2 was determined inaccurately by the conoscopic method. Therefore, it was necessary to refine the orientation of the main planes of this sample in order to perform the necessary measurements. As mentioned in the second part of this article [2], the necessary measurements to determine the optical constants of the LiNbO<sub>3</sub> crystal can be performed on any plane perpendicular to the (001) plane. Therefore, it was only necessary to refine the orientation of the (001) plane and prepare for measurements any plane perpendicular to it. Thus, we confirmed by direct measurements that for the implementation of the proposed combined ellipsometric method, knowledge of the crystallographic orientation of the crystal under study is completely optional. Moreover, the method itself in many cases makes it possible to determine or refine this crystallographic orientation. It is clear that this does not apply to crystals of the monoclinic and, especially, triclinic system. In these crystals, the orientation of the optical indicatrix does not coincide with the crystallographic orientation of the crystal [45]. A quite logical question may arise: how confident can we be in the orientation of the LiNbO<sub>3</sub> crystal sample determined by our method in order to give preference to it over the conoscopic method? The answer to this question could only be given by the results of measurements of the studied samples. In particular, tables 1 and 2 present the results of determining the optical constants of samples LN-P2 and LN-DM5. The results for sample LN-P1 were published in the second part of the article (see Table 1 in [2]). As in [2], the values of  $n$  and  $k$  given in Tables 1 and 2 are the average values of the corresponding ranges, the boundaries of which are indicated in brackets. Thus, the numbers in brackets determine the range of  $n$  and  $k$  values that satisfies the measured set of  $\Psi$  and  $\Delta$  values (and for uniaxial crystals, these are two pairs of  $\Psi$  and  $\Delta$  values), taking into account the measurement accuracy. Let's explain this with an example. We fix, for example, in Table 1 for the angle of incidence  $\varphi = 55^\circ 00'$  the values of  $n_e$ ,  $k_o$  and  $k_e$  are at the level of average values. Then the value of  $n_o$  can vary from 2.2454 to 2.2458, and all these sets of values  $n_o$ ,  $n_e$ ,  $k_o$  and  $k_e$  will satisfy the measured set of  $\Psi$  and  $\Delta$  values. In other words, the numbers in parentheses actually indicate the sensitivity of a given method. Recall that we called it the local measurement accuracy for each angle of incidence in a certain measurement configuration, since the measurements were performed at one point on the surface (for more details, see [2]). It is to demonstrate local accuracy that we use the presentation of measurement results in the form of tables. Only this form gives a complete picture of the accuracy of determining the optical constants of the crystal. In addition, it makes it possible to identify certain changes in this accuracy (for example, an increase in accuracy if the angle of incidence is close to the Brewster angle). For comparison, all these results are also presented graphically in Fig.2.

Table 1.

The principal refractive indices of the LiNbO<sub>3</sub> crystal (sample LN-P2) and the values of birefringence  $\Delta n$ , determined from the results of measurements in the configuration shown in Fig.3 [2].

Angle of incidence, $\varphi$	Principal refractive indices (wavelength $\lambda = 632.8$ nm)		Birefringence values, $\Delta n = n_e - n_o$
45°00′	$N_o = n_o - i \cdot k_o$	$2.2472(\pm 0.0002) - i \cdot 0.1119(\pm 0.0002)$	- 0.0497 ( $\pm 0.0002$ )
	$N_e = n_e - i \cdot k_e$	$2.1975(\pm 0.0002) - i \cdot 0.0677(\pm 0.0001)$	
47°30′	$N_o = n_o - i \cdot k_o$	$2.24639(\pm 0.00001) - i \cdot 0.1128(\pm 0.0001)$	- 0.0491 ( $\pm 0.00001$ )
	$N_e = n_e - i \cdot k_e$	$2.19729(\pm 0.00001) - i \cdot 0.0707(\pm 0.0001)$	
50°00′	$N_o = n_o - i \cdot k_o$	$2.2454(\pm 0.0001) - i \cdot 0.1226(\pm 0.0001)$	- 0.0482 ( $\pm 0.0002$ )
	$N_e = n_e - i \cdot k_e$	$2.1972(\pm 0.0001) - i \cdot 0.0708(\pm 0.0001)$	
52°30′	$N_o = n_o - i \cdot k_o$	$2.2451(\pm 0.0004) - i \cdot 0.1128(\pm 0.0001)$	- 0.0489 ( $\pm 0.0002$ )
	$N_e = n_e - i \cdot k_e$	$2.1962(\pm 0.0004) - i \cdot 0.0707(\pm 0.0001)$	
55°00′	$N_o = n_o - i \cdot k_o$	$2.2456(\pm 0.0002) - i \cdot 0.11275(\pm 0.00010)$	- 0.0499 ( $\pm 0.0002$ )
	$N_e = n_e - i \cdot k_e$	$2.1957(\pm 0.0004) - i \cdot 0.07048(\pm 0.00012)$	
57°30′	$N_o = n_o - i \cdot k_o$	$2.2442(\pm 0.0004) - i \cdot 0.11210(\pm 0.00008)$	- 0.0493 ( $\pm 0.0002$ )
	$N_e = n_e - i \cdot k_e$	$2.1949(\pm 0.0004) - i \cdot 0.06996(\pm 0.00008)$	
60°00′	$N_o = n_o - i \cdot k_o$	$2.2451(\pm 0.0002) - i \cdot 0.11310(\pm 0.00005)$	- 0.0494 ( $\pm 0.0002$ )
	$N_e = n_e - i \cdot k_e$	$2.1957(\pm 0.0003) - i \cdot 0.07176(\pm 0.00005)$	

Let us analyze the obtained results of measurements of the optical constants of LiNbO<sub>3</sub>, comparing them with the results of other researchers. Recall the values of the optical constants of undoped LiNbO<sub>3</sub> (sample LN-P1; see Table 1 in [2]):

$$\begin{aligned}
 N_o &= n_o - i \cdot k_o = 2.280(\pm 0.003) - i \cdot 0.0712(\pm 0.0015), \\
 N_e &= n_e - i \cdot k_e = 2.202(\pm 0.002) - i \cdot 0.0465(\pm 0.0005), \\
 \Delta n &= n_e - n_o = - 0.0775(\pm 0.0015) .
 \end{aligned}$$

These values are obtained by averaging the values of  $N_o$ ,  $N_e$ , and  $\Delta n$  over the entire measurement range. If we compare these results with the values  $n_o$ ,  $n_e$ ,  $\Delta n$  in other works [4, 20-29], then the coincidence of these values is obvious. Already in one of the first works [4], devoted to the study of LiNbO<sub>3</sub>, the following data are induced:  $n_o = 2.2967$ ,  $n_e = 2.2082$  (for  $\lambda=600$  nm),  $n_o = 2.2716$ ,  $n_e = 2.1874$  (for  $\lambda=700$  nm). In another work of the same period [20], the following results were obtained:  $n_o = 2.2862$ ,  $n_e = 2.1964$  (for  $\lambda=650$  nm),  $n_o = 2.2756$ ,  $n_e = 2.1874$  (for  $\lambda=700$  nm). Later works presented the following data:  $n_o = 2.2835$ ,  $n_e = 2.2002$  (for  $\lambda=643.85$  nm) [22],  $n_o = 2.2862$ ,  $n_e = 2.2004$  (for  $\lambda=632.8$  nm) [23]. In [27], the dependence of

the refractive indices  $n_o$  and  $n_e$  on the content of  $\text{Li}_2\text{O}$  in the melt was studied. It is shown that, in an undoped  $\text{LiNbO}_3$  crystal, the value of  $n_o$  practically does not change in the composition range 47.0–50.0 mol.%  $\text{Li}_2\text{O}$ , and is equal to  $n_o \approx 2.28$ . At the same time, the value of  $n_e$  decreases from  $\approx 2.22$  for 47.0 mol.%  $\text{Li}_2\text{O}$  to  $\approx 2.19$  for 50.0 mol.%  $\text{Li}_2\text{O}$ . As can be seen, in the case of an undoped  $\text{LiNbO}_3$  crystal, we obtained a very good agreement between our  $n_o$ ,  $n_e$ , and  $\Delta n$  values and the data of other works.

Table 2.

The principal refractive indices of the  $\text{LiNbO}_3$  crystal (sample LN-DM5) and the values of birefringence  $\Delta n$ , determined from the results of measurements in the configuration shown in Fig.3 [2].

Angle of incidence, $\varphi$	Principal refractive indices (wavelength $\lambda = 632.8$ nm)		Birefringence values, $\Delta n = n_e - n_o$
45°00′	$N_o = n_o - i \cdot k_o$	$2.24596(\pm 0.00004) - i \cdot 0.0786(\pm 0.0002)$	– 0.06994 ( $\pm 0.0001$ )
	$N_e = n_e - i \cdot k_e$	$2.17602(\pm 0.00004) - i \cdot 0.0494(\pm 0.0001)$	
47°30′	$N_o = n_o - i \cdot k_o$	$2.2447(\pm 0.0004) - i \cdot 0.0922(\pm 0.0001)$	– 0.0683 ( $\pm 0.0002$ )
	$N_e = n_e - i \cdot k_e$	$2.1764(\pm 0.0003) - i \cdot 0.06725(\pm 0.00005)$	
50°00′	$N_o = n_o - i \cdot k_o$	$2.2449(\pm 0.0002) - i \cdot 0.09175(\pm 0.00005)$	– 0.0694 ( $\pm 0.0002$ )
	$N_e = n_e - i \cdot k_e$	$2.1755(\pm 0.0003) - i \cdot 0.0662(\pm 0.0001)$	
52°30′	$N_o = n_o - i \cdot k_o$	$2.24395(\pm 0.00005) - i \cdot 0.09178(\pm 0.00002)$	– 0.0685 ( $\pm 0.0001$ )
	$N_e = n_e - i \cdot k_e$	$2.17570(\pm 0.00015) - i \cdot 0.06626(\pm 0.00004)$	
55°00′	$N_o = n_o - i \cdot k_o$	$2.2438(\pm 0.0003) - i \cdot 0.09110(\pm 0.00005)$	– 0.0687 ( $\pm 0.0002$ )
	$N_e = n_e - i \cdot k_e$	$2.1751(\pm 0.0002) - i \cdot 0.06615(\pm 0.00005)$	
57°30′	$N_o = n_o - i \cdot k_o$	$2.2434(\pm 0.0003) - i \cdot 0.09095(\pm 0.00005)$	– 0.0684 ( $\pm 0.0002$ )
	$N_e = n_e - i \cdot k_e$	$2.1750(\pm 0.0003) - i \cdot 0.06685(\pm 0.00005)$	
60°00′	$N_o = n_o - i \cdot k_o$	$2.2432(\pm 0.0002) - i \cdot 0.09140(\pm 0.00005)$	– 0.0682 ( $\pm 0.0002$ )
	$N_e = n_e - i \cdot k_e$	$2.1750(\pm 0.0001) - i \cdot 0.06825(\pm 0.00005)$	

Before analyzing the results obtained for the other two samples, one important circumstance should be emphasized. Samples LN-P1 and LN-P2 are made from crystals grown using the same technology in the same laboratory. The only difference between them is that sample LN-P2 was additionally heat treated. Sample LN-DM5 was also grown using the same technology, but was alloyed from the melt with an MgO impurity. If we average the values  $n_o$ ,  $n_e$ ,  $\Delta n$  for samples LN-P2 and LN-DM5 (Tables 1 and 2) over the entire measurement range, then with slight rounding we get the following results. For sample LN-P2:

$$\begin{aligned}
 N_o = n_o - i \cdot k_o &= 2.2455(\pm 0.0015) - i \cdot 0.0712(\pm 0.0015), \\
 N_e = n_e - i \cdot k_e &= 2.1965(\pm 0.0015) - i \cdot 0.0465(\pm 0.0005), \\
 \Delta n = n_e - n_o &= -0.049(\pm 0.001).
 \end{aligned}$$

And for sample LN-DM5:

$$N_o = n_o - i \cdot k_o = 2.2445(\pm 0.0015) - i \cdot 0.0712(\pm 0.0015),$$

$$N_e = n_e - i \cdot k_e = 2.1757(\pm 0.0007) - i \cdot 0.0465(\pm 0.0005),$$

$$\Delta n = n_e - n_o = -0.069(\pm 0.001).$$

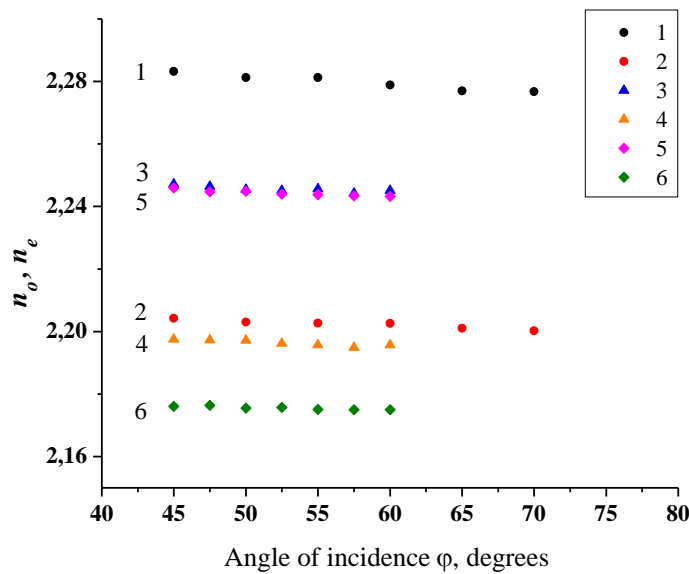


Fig.2. Dependences of the ordinary ( $n_o$ ) and extraordinary ( $n_e$ ) refractive indices on the angle of incidence of the laser beam for the investigated LiNbO<sub>3</sub> crystals: 1 –  $n_o$  and 2 –  $n_e$  (sample LN-P1), 3 –  $n_o$  and 4 –  $n_e$  (sample LN-P2), 5 –  $n_o$  and 6 –  $n_e$  (sample LN-DM5).

As we can see, the values of the optical constants for these two samples differ significantly from the values for the sample LN-P1 (Fig.2). In particular, for the sample LN-P2, the usual refractive index [ $n_o = 2.2455(\pm 0.0015)$ ] is much lower than that of the as grown LiNbO<sub>3</sub> crystal (sample LN-P1). As a result, the value of birefringence [ $\Delta n = -0.049(\pm 0.001)$ ] is also much lower. For the sample LN-DM5, the value of birefringence [ $\Delta n = -0.069(\pm 0.001)$ ] is only slightly less than that of the as grown LiNbO<sub>3</sub> crystal. However, in this case, the values of the ordinary [ $n_o = 2.2445(\pm 0.0015)$ ] and extraordinary [ $n_e = 2.1757(\pm 0.0007)$ ] refractive indices are significantly lower than those of the as grown LiNbO<sub>3</sub> crystal. First, this begs the question: did we make a mistake somewhere when applying the combined ellipsometric method? For example, these results may be erroneous due to inaccurate determination of the orientation of the optical indicatrix. We can answer this remark in the following way. Applying certain optical models to analyze the data of ellipsometric measurements, we were convinced that the most reliable way to check the correctness of their use is the use of a multi-angle measurement technique. That is why we performed measurements in a fairly wide range of the angle of incidence  $\varphi$ . An error in determining the orientation of the optical indicatrix with a high probability would lead to the appearance of a pronounced dependence of the values of the optical constants

$n_o$ ,  $n_e$ ,  $\Delta n$  on the angle of incidence  $\varphi$ . But nothing of the kind is observed for samples LN-P2 and LN-DM5 (Fig. 2). In addition, applying the same method to the sample LN-P1 gave very good results. Therefore, it should obviously be recognized that such a change in the values of the optical constants of the crystals under study is the result of a change in their properties. What are the reasons for such changes? Apparently, the main reason for such significant changes is high-temperature annealing in an  $H_2O$  atmosphere. This conclusion stems from the fact that these changes occurred in both samples: undoped and doped with MgO. However, let us first analyze the effect of magnesium doping on the optical properties of  $LiNbO_3$ . For example, in [25], for a  $LiNbO_3$  crystal doped with MgO (5 mol.%), the following results were obtained:  $n_o = 2.2792$ ,  $n_e = 2.1916$  (for  $\lambda=632.8$  nm). In [27], the dependence of the refractive indices  $n_o$  and  $n_e$  on the Mg content in the melt was also studied. It is shown that, in a doped  $LiNbO_3$  crystal, the  $n_o$  value smoothly decreases from  $\approx 2.285$  for 1.5 mol.% Mg to  $\approx 2.275$  for 8.0 mol.%  $Li_2O$ . At the same time, the value of  $n_e$  decreases from  $\approx 2.205$  for 1.5 mol.% Mg to  $\approx 2.19$  for 5.0 mol.% Mg, and again increases to  $\approx 2.195$  for 8.0 mol.% Mg (for  $\lambda=633$  nm). If we compare the dispersion dependences  $n_o = f(\lambda)$  and  $n_e = f(\lambda)$  given in [46], then it is also easy to notice a slight decrease in the values of  $n_o$  and  $n_e$  in  $LiNbO_3$ : Mg compared to undoped lithium niobate. It would be possible to cite data from other works, but the general conclusion is obvious: doping  $LiNbO_3$  crystals with magnesium leads to some decrease in the values of  $n_o$  and  $n_e$ . However, the values obtained by us for the sample LN-DM5 are significantly lower than those given now from other works. Thus, doping alone could not have such a significant effect on the change in the optical constants of the sample LN-DM5. And since the same significant changes in  $n_o$ ,  $n_e$ ,  $\Delta n$  were obtained for the undoped sample LN-P2, the only reason for this can only be high-temperature annealing. Surprisingly, none of the works that studied the effect of high-temperature annealing on the optical properties of  $LiNbO_3$  [34–41] contain data on the values of the main optical constants of annealed  $LiNbO_3$  crystalline samples. It seems that the authors of these works apriority consider such changes impossible. As mentioned earlier, we cannot draw any conclusions on the basis of only ellipsometric measurements about the possible physical mechanisms that could cause the changes in optical constants that we have obtained. It could be assumed that one of the possible reasons could be a change in the properties of the near-surface layers of the samples under study due to annealing. But in this case, the multiangle technique of ellipsometric measurements should also reveal this feature. The fact is that in this case the optical model used for the analysis of measurements does not fully correspond to the object of study. And this would necessarily manifest itself in a clear change in the values of the optical constants of the samples with a change in the angle of incidence. But as can be seen from Fig. 2, the dependences  $n_o = f(\varphi)$  and  $n_e = f(\varphi)$  are practically ideal straight lines parallel to the abscissa axis. Therefore, to answer the question about the reasons that caused such significant changes in the optical constants of the studied samples of lithium niobate ( $LiNbO_3$ ) crystals, additional studies using other methods are required.

#### 4. Conclusions

Thus, in the fourth part of the article, the application of the proposed method for the complete optical characterization of crystals to optically uniaxial crystals is considered. Lithium niobate ( $LiNbO_3$ ) crystals became the object of research. Refining the orientation of the optical indicatrix in the samples under study, we confirmed by direct measurements the conclusion made earlier [1] that the knowledge of the crystallographic orientation of the crystal under study is absolutely not necessary for the implementation of the proposed combined ellipsometric method. Moreover, the method itself in many cases makes it possible to determine or refine



this crystallographic orientation. The obtained values of the optical constants of the undoped LiNbO<sub>3</sub> crystal [ $n_o = 2.280(\pm 0.003)$ ,  $n_e = 2.202(\pm 0.002)$ ,  $\Delta n = -0.0775(\pm 0.0015)$ ] fully confirmed the correctness of the proposed method and its efficiency in the study of uniaxial crystals. To test the sensitivity of the combined ellipsometric method, we also studied LiNbO<sub>3</sub> crystals subjected to high-temperature annealing in an H<sub>2</sub>O atmosphere. The optical constants obtained for an undoped LiNbO<sub>3</sub> crystal [ $n_o = 2.2455(\pm 0.0015)$ ,  $n_e = 2.1965(\pm 0.0015)$ ,  $\Delta n = -0.049(\pm 0.001)$ ] and a magnesium-doped LiNbO<sub>3</sub> crystal [ $n_o = 2.2445(\pm 0.0015)$ ,  $n_e = 2.1756(\pm 0.0007)$ ,  $\Delta n = -0.069(\pm 0.001)$ ], show a significant decrease in the values of optical constants compared to the as grown crystal. Apparently, the main reason for such significant changes is high-temperature annealing in an H<sub>2</sub>O atmosphere. But even if this is not entirely accurate, it does not change anything for evaluating the effectiveness of the application of the method itself. Our main goal was to show the applicability of the method to the analysis of possible changes in the optical constants of a crystal caused by the influence of various factors on its properties. The results obtained show that our goal has been achieved.

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**КОМБІНОВАНА ЕЛІПСОМЕТРИЧНА МЕТОДИКА ПОВНОЇ ОПТИЧНОЇ  
ХАРАКТЕРИЗАЦІЇ КРИСТАЛІВ.  
IV. ЗАСТОСУВАННЯ ДО ОДНОВІСНИХ КРИСТАЛІВ**

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У четвертій частині статті розглянуто застосування запропонованої еліпсометричної методики повної оптичної характеристики кристалів до оптично одновісних кристалів. Об'єктом дослідження стали кристали ніобату літію ( $\text{LiNbO}_3$ ). Уточнюючи орієнтацію оптичної індикатриси в досліджуваних зразках, ми прямими вимірюваннями підтвердили висновок, зроблений у першій частині статті, що для практичної реалізації комбінованої еліпсометричної методики знання кристалографічної орієнтації досліджуваного кристала зовсім необов'язкове. Більше того, сама методика в багатьох випадках дає змогу визначити або уточнити кристалографічну орієнтацію зразка. Одержані значення оптичних констант нелегованого кристала  $\text{LiNbO}_3$  [ $n_o = 2.280(\pm 0.003)$ ,  $n_e = 2.202(\pm 0.002)$ ,  $\Delta n = -0.0775(\pm 0.0015)$ ] цілковито підтвердили коректність запропонованої методики та її ефективність при дослідженні одновісних кристалів. Для перевірки чутливості комбінованої еліпсометричної методики ми дослідили також кристали  $\text{LiNbO}_3$ , піддані високотемпературному відпалу в атмосфері  $\text{H}_2\text{O}$ . Одержані значення оптичних констант нелегованого кристала  $\text{LiNbO}_3$  [ $n_o = 2.2455(\pm 0.0015)$ ,  $n_e = 2.1965(\pm 0.0015)$ ,  $\Delta n = -0.049(\pm 0.001)$ ] і легovanого магнієм кристала  $\text{LiNbO}_3$  [ $n_o = 2.2445(\pm 0.0015)$ ,  $n_e = 2.1756(\pm 0.0007)$ ,  $\Delta n = -0.069(\pm 0.001)$ ] є суттєво менше значень таких оптичних констант вихідного кристала. Найбільш імовірною причиною, яка могла викликати такі суттєві зміни, є високотемпературний відпал в атмосфері  $\text{H}_2\text{O}$ . Такий висновок, безперечно, потребує перевірки шляхом дослідження цих кристалів іншими методами. Але навіть, якщо цей висновок і не зовсім точний, то це нічого не змінює в оцінці ефективності застосування самої методики. Нашою основною метою було показати застосовність методики для аналізу можливих змін оптичних констант кристала, зумовлених впливом різних чинників на його властивості. Одержані результати показують, що поставлена нами мета досягнута.

*Ключові слова:* еліпсометрія, оптична індикатриси, головні показники заломлення, одновісні кристали, ніобат літію.

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