ISSN 2224-087X. Електроніка та інформаційні технології. 2021. Випуск 16. С. 104–117
Electronics and information technologies. 2021. Issue 16. P. 104–117

UDK codes: 535.321; 535.391.4; 535.515; 535.524; 548.1.022/025; 548.1.025/027.
OCIS codes: 120.0120; 120.2130; 240.0240; 240.2130; 260.0260; 260.1180; 260.1440; 260.2130.
DOI: https://doi.org/10.30970/eli.16.11

# THE COMBINED ELLIPSOMETRIC METHOD OF COMPLETE OPTICAL CHARACTERIZATION OF CRYSTALS. II. DETERMINATION OF THE OPTICAL CONSTANTS OF CRYSTAL

Victor Belyukh, Bohdan Pavlyk

*Faculty of Electronics and Computer Technologies,*
*Ivan Franko National University of Lviv,*
*107 Tarnavsky St., UA–79017 Lviv, Ukraine*
*belyukh@electronics.lnu.edu.ua*

This part of the article describes the second stage of the combined ellipsometric method of complete optical characterization of crystals. The testing of the second stage was carried out on crystals of lithium niobate ($LiNbO_3$) and cadmium tungstate ($CdWO_4$). The obtained results of measurements of an optically uniaxial $LiNbO_3$ crystal fully confirmed the correctness of the proposed method and its applicability for optical characterization of crystals. In particular, the values of the principal refractive indices {$n_o = 2.280(\pm 0.003)$, $n_e = 2.202(\pm 0.002)$} and birefringence {$\Delta n = -0.0775(\pm 0.0015)$} of the $LiNbO_3$ crystal are in good agreement with the values of these quantities, obtained by other researchers by other methods. Studies of the optically biaxial $CdWO_4$ crystal were important for analyzing the accuracy of determining the optical constants. For generality of this analysis, measurements were performed in different measurement configurations at several angles of incidence of the laser beam. In particular, according to the results of measurements in two configurations (angle of incidence 45°), the following values of the principal refractive indices of the $CdWO_4$ crystal (doped from the melt 0.375 wt.% PbO) were obtained: $n_g = 2.249 \pm 0.002$, $n_m = 2.185 \pm 0.002$, $n_p = 2.130 \pm 0.008$. Based on these values of $n_g$, $n_m$, and $n_p$, the angle between the optical axes and the optical sign of the crystal were determined. It has been shown experimentally that the $CdWO_4$ crystal is a pronounced biaxial crystal with an angle between the optical axes close to 90°. Possible ways to improve the accuracy of determining the optical constants of crystals are also analyzed.

*Key words*: ellipsometry, optical indicatrix, principal refractive indexes, uniaxial and biaxial crystals.

## 1. Introduction

In the first part of this article [1], a method for determining the orientation of the optical indicatrix in crystals was described in detail. This method became the basis for the combined ellipsometric method for complete optical characterization of crystals and its first stage. In the second part of the article, we show how to determine the optical constants of a particular crystal, knowing the orientation of the optical indicatrix and using the relations obtained by R. H. W. Graves [2]. This is the second stage of the described combined ellipsometric method. It should be said that the research results presented in the second part of the article have already been partially published in the first attempt to describe the method under consideration [3]. But, firstly, at that time, for various reasons, this plan was not fully realized. Secondly, these results are absolutely necessary for a complete description of the combined method. Thirdly, article [3] was published in Ukrainian, and therefore may not be available for everyone to understand. In addition, we significantly changed the notation system used in [3], and introduced a number of clarifications. This was necessary to create a complete picture of the combined ellipsometric method.

## 2. Ellipsometric measurement technique and determination optical constants of the crystal

The second stage of the combined ellipsometric method consists of the following parts:

a) preparation of high-quality crystal surfaces that correspond to the principal cross sections of the optical indicatrix;

b) performing the required number of ellipsometric measurements on these planes;

c) determination of the principal refractive indices of the crystal by solving the corresponding system of equations.

Since in the case of an optically biaxial crystal (and these are crystals of the rhombic, monoclinic and triclinic systems), it is necessary to determine three principal refractive indices ($N_1$, $N_2$, $N_3$), then three measurements should be performed in at least two principal cross sections of the optical indicatrix. Since the triaxial ellipsoid (which is the optical indicatrix of such crystals) has three principal elliptical cross sections, there are 20 possible measurement configurations obtained by combination of the measurements in these principal cross sections. If measurements are performed only at one angle of incidence of the beam on the surface of the crystal, then, strictly speaking, it is sufficient to prepare for measurements only two of the three principal cross sections of the optical indicatrix. But, undoubtedly, in order to be sure of the correctness of the obtained values of $N_1$, $N_2$, $N_3$, it is necessary to prepare for measurements all three principal cross sections of the optical indicatrix. After that, having performed measurements in several measuring configurations, it will be possible to make a comparative analysis of the results obtained. Fig.1 shows one of the possible configurations for ellipsometric measurements of an optically biaxial crystal. Note that $\boldsymbol{XYZ}$ is the coordinate system associated with the ellipsometer ($\boldsymbol{YOX}$ is the plane of incidence of the laser beam), and $\boldsymbol{N_1N_2N_3}$ is the coordinate system of the optical indicatrix. To eliminate confusion with the principal refractive indices, the axes of the coordinate systems are denoted in bold. In this case (Fig.1), two measurements are performed in the crystal plane, which corresponds to the principal section of the optical indicatrix $\boldsymbol{N_1ON_3}$ (Fig.1a, b), and one in the plane, which corresponds to the principal cross section $\boldsymbol{N_1ON_2}$ (Fig.1c). Having performed all the necessary measurements, we obtain three pairs of ellipsometric parameters (angles) $\Psi$ and $\Delta$, which are related to the principal refractive indices of the crystal by the basic ellipsometry equation [2]:

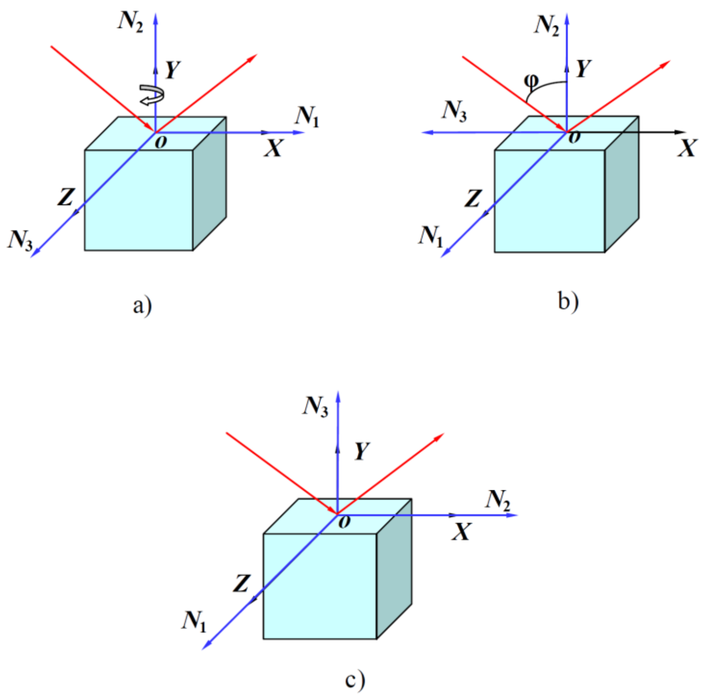



Fig.1. Configuration of ellipsometric measurements of an optically biaxial crystal to determine its principal refractive indices. Measurement configuration symbol: ***N*₁*X*–*N*₂*Y*–*N*₃*Z*** (a), ***N*₁*Z*–*N*₂*Y*–*N*₃*X*** (b), ***N*₁*Z* – *N*₂*X*– *N*₃*Y*** (c). Laser beam incidence plane: ***YOX***. φ is the angle of incidence.

$$tg\,\Psi_1\cdot e^{i\Delta_1}=\frac{\left(\sqrt{N_2^2-\sin^2\varphi}-N_1N_2\cos\varphi\right)\cdot\left(\cos\varphi+\sqrt{N_3^2-\sin^2\varphi}\right)}{\left(\sqrt{N_2^2-\sin^2\varphi}+N_1N_2\cos\varphi\right)\cdot\left(\cos\varphi-\sqrt{N_3^2-\sin^2\varphi}\right)}\,, \tag{1}$$

$$tg\,\Psi_2\cdot e^{i\Delta_2}=\frac{\left(\sqrt{N_2^2-\sin^2\varphi}-N_3N_2\cos\varphi\right)\cdot\left(\cos\varphi+\sqrt{N_1^2-\sin^2\varphi}\right)}{\left(\sqrt{N_2^2-\sin^2\varphi}+N_3N_2\cos\varphi\right)\cdot\left(\cos\varphi-\sqrt{N_1^2-\sin^2\varphi}\right)}\,, \tag{2}$$

$$tg\,\Psi_3\cdot e^{i\Delta_3}=\frac{\left(\sqrt{N_3^2-\sin^2\varphi}-N_2N_3\cos\varphi\right)\cdot\left(\cos\varphi+\sqrt{N_1^2-\sin^2\varphi}\right)}{\left(\sqrt{N_3^2-\sin^2\varphi}+N_2N_3\cos\varphi\right)\cdot\left(\cos\varphi-\sqrt{N_1^2-\sin^2\varphi}\right)}\,. \tag{3}$$

Thus, we obtain a system of three nonlinear transcendental equations {(1) – (3)} in complex form, which we solve for the complex refractive indices $N_1$, $N_2$, $N_3$. This system of equations cannot be solved analytically. Therefore, to solve it, it is necessary to use numerical methods. Since the equations {(1) – (3)} are complex, it is obviously easier to solve them just as complex equations. To do this, you should use programming languages that provide complex arithmetic procedures.

As an example of the practical implementation of the second stage of the combined ellipsometric method, let us consider a specific case of a $CdWO_4$ crystal. The orientation of the optical indicatrix of this crystal for the wavelength $\lambda$ = 632.8 nm was determined in the first part of this article [1]. Since all the designations of the principal axes of the indicatrix have already been fulfilled earlier ($N_1 = N_m$, $N_2 = N_p$, $N_3 = N_g$ [1]), we will immediately use them. Fig.2 shows one of the possible configurations for ellipsometric measurements of an optically biaxial $CdWO_4$ crystal.

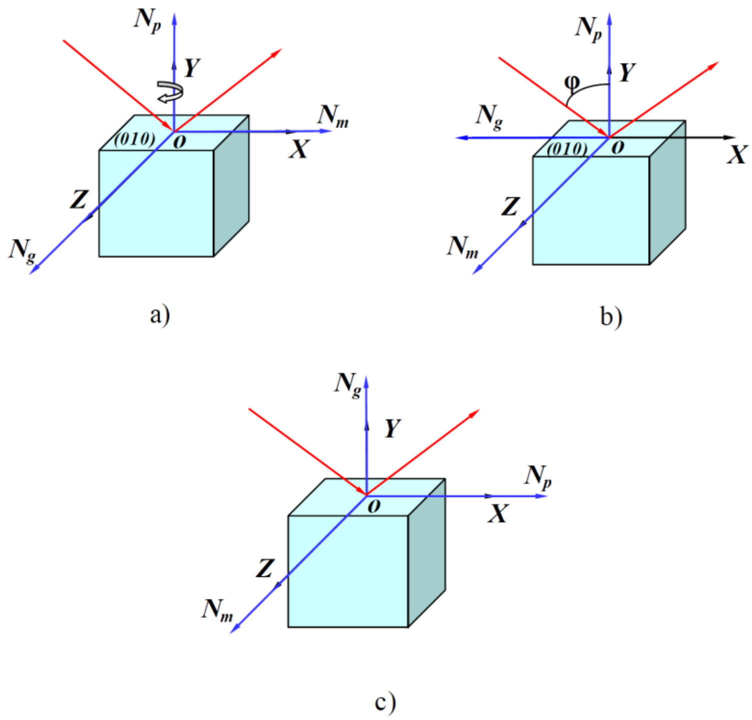



Fig.2. Configuration of ellipsometric measurements of an optically biaxial $CdWO_4$ crystal to determine its principal refractive indices. Measurement configuration symbol: $\boldsymbol{N_mX}$–$\boldsymbol{N_pY}$–$\boldsymbol{N_gZ}$ (a), $\boldsymbol{N_mZ}$–$\boldsymbol{N_pY}$–$\boldsymbol{N_gX}$ (b), $\boldsymbol{N_mZ}$ – $\boldsymbol{N_pX}$– $\boldsymbol{N_gY}$ (c). $\boldsymbol{N_mN_pN_g}$ – optical indicatrix coordinate system.

We emphasize that, in the general case, the coordinate system of the optical indicatrix $\boldsymbol{N_gN_mN_p}$ is in no way related to the crystallographic coordinate system of the sample under study. That is why knowledge of the crystallographic orientation of the sample is completely optional when implementing our method. Thus, in this configuration, two measurements are performed on the plane (010) of the $CdWO_4$ crystal (Fig.2a, b). The third measurement is performed on a plane that is perpendicular to the plane (010) and rotated relative to the plane (100) by approximately 19° (Fig.2c). Having performed all the necessary measurements, we obtain three pairs of ellipsometric parameters (angles) Ψ and Δ, which are related to the principal refractive indices of the crystal by the basic ellipsometry equation:

$$tg\,\Psi_1 \cdot e^{i\Delta_1} = \frac{\left(\sqrt{N_p^2 - \sin^2\varphi} - N_m N_p \cos\varphi\right)\cdot\left(\cos\varphi + \sqrt{N_g^2 - \sin^2\varphi}\right)}{\left(\sqrt{N_p^2 - \sin^2\varphi} + N_m N_p \cos\varphi\right)\cdot\left(\cos\varphi - \sqrt{N_g^2 - \sin^2\varphi}\right)}\ , \tag{4}$$

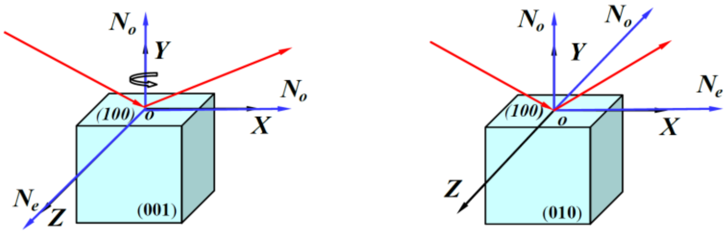
$$tg\,\Psi_2 \cdot e^{i\Delta_2} = \frac{\left(\sqrt{N_p^2 - \sin^2\varphi} - N_g N_p \cos\varphi\right)\cdot\left(\cos\varphi + \sqrt{N_m^2 - \sin^2\varphi}\right)}{\left(\sqrt{N_p^2 - \sin^2\varphi} + N_g N_p \cos\varphi\right)\cdot\left(\cos\varphi - \sqrt{N_m^2 - \sin^2\varphi}\right)}\ , \tag{5}$$

$$tg\,\Psi_3 \cdot e^{i\Delta_3} = \frac{\left(\sqrt{N_g^2 - \sin^2\varphi} - N_p N_g \cos\varphi\right)\cdot\left(\cos\varphi + \sqrt{N_m^2 - \sin^2\varphi}\right)}{\left(\sqrt{N_g^2 - \sin^2\varphi} + N_p N_g \cos\varphi\right)\cdot\left(\cos\varphi - \sqrt{N_m^2 - \sin^2\varphi}\right)}\ . \tag{6}$$

Thus, for the chosen configuration of measurements of the $CdWO_4$ crystal (Fig.2), we obtain a system of three nonlinear transcendental equations {(4) – (6)} in a complex form, by solving which we find the principal refractive indices $N_g$, $N_m$, $N_p$.

In optically uniaxial crystals, the situation is somewhat different. The optical indicatrix of uniaxial crystals is a uniaxial ellipsoid, the axis of rotation of which coincides with the axis of symmetry of the crystal and is the only optical axis of the crystal. Therefore, the orientation of the optical indicatrix is determined only by the direction of the principal symmetry axis of the crystal. In such crystals, the orientation of the optical axis is completely determined by the crystal symmetry: the optical axis is always the [001] or [0001] direction. The only circular section of the optical indicatrix is perpendicular to the principal symmetry axis of the crystal and has a radius of $N_o$. In this case, it is necessary to perform only two ellipsometric measurements on any plane in which the optical axis of the crystal lies. Fig.3 shows a possible measurement configuration for a particular crystal – lithium niobate ($LiNbO_3$). In this case, we are making both measurements on the plane (100). In the first measurement, the optical axis of the crystal is perpendicular to the plane of incidence of the beam (Fig.3a), and in the second, it is parallel (Fig.3b). But, let us emphasize again, the choice of the plane (100) is completely optional. In this particular case of a $LiNbO_3$ crystal, it can be any other plane perpendicular to the plane (001). To designate the measurement configuration, we additionally introduce two more axes $\boldsymbol{N_o}$ of the optical indicatrix, aligning them with the corresponding axes of the crystallographic coordinate system. But this is a completely formal step, since in uniaxial crystals, as we have already said, the orientation of the optical indicatrix is determined by only one axis $\boldsymbol{N_e}$.

Since uniaxial crystals are characterized by only two principal refractive indices, $N_o$ and $N_e$, we obtain a system of two equations:




a) b)

Fig.3. Configuration of ellipsometric measurements of an optically uniaxial $LiNbO_3$ crystal to determine its principal refractive indices. Measurement configuration symbol:***N<sub></sub>***$\boldsymbol{N_oX}$–$\boldsymbol{N_oY}$–$\boldsymbol{N_eZ}$ (a), $\boldsymbol{N_eX}$–$\boldsymbol{N_oY}$–$\boldsymbol{N_oZ}$ (b). $\boldsymbol{N_oN_oN_e}$ – optical indicatrix coordinate system.

$$tg\,\Psi_1\cdot e^{i\Delta_1}=\frac{\left(\sqrt{N_o^2-\sin^2\varphi}-N_o^2\cos\varphi\right)\cdot\left(\cos\varphi+\sqrt{N_e^2-\sin^2\varphi}\right)}{\left(\sqrt{N_o^2-\sin^2\varphi}+N_o^2\cos\varphi\right)\cdot\left(\cos\varphi-\sqrt{N_e^2-\sin^2\varphi}\right)}\ , \qquad (7)$$

$$tg\,\Psi_2\cdot e^{i\Delta_2}=\frac{\left(\sqrt{N_o^2-\sin^2\varphi}-N_eN_o\cos\varphi\right)\cdot\left(\cos\varphi+\sqrt{N_o^2-\sin^2\varphi}\right)}{\left(\sqrt{N_o^2-\sin^2\varphi}+N_eN_o\cos\varphi\right)\cdot\left(\cos\varphi-\sqrt{N_o^2-\sin^2\varphi}\right)}\ . \qquad (8)$$

Having solved this system of two nonlinear transcendental equations {(7), (8)}, we obtain the required principal refractive indices $N_o$ and $N_e$ in complex form. One should pay attention to one more important feature of all written equations. The system of equations {(1) – (3)} has this form for an optically biaxial crystal only for a specific measurement configuration. Changing to a different measurement configuration will change the equations. Applying equations {(1) – (3)} for a particular optically biaxial crystal, we specify their form, as, for example, in the case of the $CdWO_4$ crystal {equations (4) – (6)}. But the system of equations {(7), (8)} remains unchanged for any optically uniaxial crystal.

**3. Results of experimental ellipsometric measurements of crystals and analysis of the accuracy of determining the optical constants**

The second stage of the combined ellipsometric method was tested on optically uniaxial $LiNbO_3$ crystals and optically biaxial $CdWO_4$ crystals. We investigated both pure crystals and crystals doped with various impurities. All measurements were performed on a LEF-3M-1 laser ellipsometer ($\lambda$ = 632.8 nm) at room temperature. First of all, we tried to get an answer to the question: what is the accuracy of determining the optical constants using this method? In addition to answering this question, it was necessary to find out exactly what factors affect this accuracy and, accordingly, propose ways to improve it.

Studies of $LiNbO_3$ crystals were important for us from the point of view of testing the very method of complete optical characterization of crystals. Since the $LiNbO_3$ crystal has been thoroughly investigated (see, for example, [4-12]), we had the opportunity to compare our results with the results obtained by other researchers using other methods. The $LiNbO_3$ crystal belongs to the trigonal system, class 3*m*, space group of symmetry *R*3*c* [4-6]. According to the data of various researchers, the parameters of the rhombohedral cell are in the ranges: $a = 0.5482 \div 0.5497$ nm, $\alpha = 55°52' \div 56°02'$; parameters of the hexagonal cell: $a = 0.5147 \div 0.5154$ nm, $c = 1.3816 \div 1.3865$ nm [6]. The dependences of the refractive indices $n_o$ and $n_e$ on wavelength, temperature, and composition have also been studied in detail (see, for example, [6–12]). Table 1 shows the results of our studies of a pure $LiNbO_3$ crystal grown at Scientific Research Company "Electron-Carat" (Lviv).

Table 1. The principal refractive indices of the $LiNbO_3$ crystal and the values of birefringence $\Delta n$, determined from the results of measurements in the configuration shown in Fig.3.

| Angle of incidence, φ | Principal refractive indices (wavelength λ = 632.8 nm) | | Birefringence values, $\Delta n = n_e - n_o$ |
|---|---|---|---|
| 45° | $N_o=n_o-i\cdot k_o$ | 2.2832(±0.0009) – $i$·0.0698(±0.0003) | – 0.0790 (±0.0005) |
| | $N_e=n_e-i\cdot k_e$ | 2.2042(±0.0009) – $i$·0.0458(±0.0003) | |
| 50° | $N_o=n_o-i\cdot k_o$ | 2.2812(±0.0007) – $i$·0.0721(±0,0003) | – 0.0782 (±0.0005) |
| | $N_e=n_e-i\cdot k_e$ | 2.2030(±0.0007) – $i$·0.0472(±0,0003) | |
| 55° | $N_o=n_o-i\cdot k_o$ | 2.2812(±0.0006) – $i$·0.0727(±0.0002) | – 0.0785 (±0.0004) |
| | $N_e=n_e-i\cdot k_e$ | 2.2027(±0.0006) – $i$·0.0471(±0.0002) | |
| 60° | $N_o=n_o-i\cdot k_o$ | 2.2789(±0.0005) – $i$·0.0718(±0.0001) | – 0.0763 (±0.0004) |
| | $N_e=n_e-i\cdot k_e$ | 2.2026(±0,0005) – $i$·0.0468(±0.0001) | |
| 65° | $N_o=n_o-i\cdot k_o$ | 2.27702(±0.00004) – $i$·0.07145(±0.00001) | – 0.07602 (±0.00004) |
| | $N_e=n_e-i\cdot k_e$ | 2.20100(±0.00001) – $i$·0.04734(±0.00001) | |
| 70° | $N_o=n_o-i\cdot k_o$ | 2.2767(±0.0005) – $i$·0.0724(±0.0001) | – 0.0765 (±0.0004) |
| | $N_e=n_e-i\cdot k_e$ | 2.2002(±0.0002) – $i$·0.0469(±0.0001) | |

To achieve generality in the analysis of the accuracy of determining the optical constants, we performed measurements at different angles of incidence of the laser beam of the ellipsometer. The values of $n$ and $k$ given in Table 1 are the average values of the respective ranges, the boundaries of which are indicated in parentheses. In other words, the numbers in parentheses actually indicate the sensitivity of this method. It could also be called local accuracy for each angle of incidence in a certain measurement configuration, since the measurements were made at one point on the crystal surface. The local accuracy (or sensitivity) of the method depends mainly on the accuracy of measuring the ellipsometric parameters Ψ and Δ. Provided that a 4-zone measurement technique is used and with the correct choice of measurement conditions on ellipsometers of the LEF-3M-1 type, the parameters Ψ and Δ can be determined with an accuracy of ±0.5'. Thus, the numbers in parentheses in Table 1 determine the range of values of $n$ and $k$ that satisfies the measured set of values of Ψ and Δ taking into account the indicated measurement accuracy. There is, however, one clarification to be made. Taking into account the structure of equations {(7), (8)}, it is obvious that the values of the complex refractive indices $N_o$ and $N_e$ are interrelated. Therefore, in the corresponding ranges of local accuracy, both the refractive indices $n_o$ and $n_e$ and the extinction coefficients $k_o$ and $k_e$ cannot simultaneously take diametrically opposite values (for example, $n_o$ is the maximum value, and $n_e$ is the minimum). It is for this reason that the local accuracy of this method for the value of birefringence $\Delta n$ is somewhat different than for $n_o$ and $n_e$ (Table 1).

As expected, near the Brewster angle (and for $LiNbO_3$ it is ≈64º) the sensitivity of the method sharply increases (see Table 1). It would seem that this immediately determines the range of angles of incidence at which measurements should be made. However, everything is not so simple here. If we compare the values of $n_o$ and $n_e$ given in Table 1 with data from other sources, it is easy to see that it is at angles of incidence of 45÷55º that the values of $n_o$ and $n_e$ practically coincide with the values, given, for example, in the reference book [6] and works [7-12]. In our opinion, the most probable reason for the decrease in $n_o$ and $n_e$ with an increase in the angle of incidence φ is as follows. On the investigated surface of the crystal, subjected to mechanical and chemical treatment, there is always a damaged layer, the properties of which differ significantly from the bulk properties of the crystal. Therefore, strictly speaking, there arises a certain discrepancy between the "optically isotropic homogeneous medium - optically anisotropic homogeneous crystal" model (which we use to calculate $N_o$ and $N_e$) with the real object of research. As the angle of incidence increases, the area of interaction of the laser beam with the crystal surface increases. Consequently, the role of the damaged layer in the formation of the reflected beam increases. Accordingly, the discrepancy between the optical model and the real object of research also increases, which leads to a decrease in the values of $n_o$ and $n_e$. Taking into account the aforesaid, when studying crystals on ellipsometers of the LEF-3M-1 type, one should, apparently, choose an angle of incidence in the range of 45÷55º.

If we carry out averaging over all the values given in Table 1 and determine the boundaries of deviations from the mean values, then we can introduce the concept of integral accuracy. Thus, with small roundings, we get:

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

As we can see, even in this general case, the accuracy of determining the principal optical constants of $LiNbO_3$ remains rather high. Obviously, the integral accuracy, determined from the results of measurements at different angles of incidence and in different measuring configurations, will always be less than the local accuracy. However, the higher the quality of the crystal surfaces under study, the more precisely the orientation of the optical indicatrix was determined, the higher will be the integral accuracy of determining the optical constants. It should be said that it is the results of the optical characterization of the $LiNbO_3$ crystal that have become convincing proof of the correctness of this ellipsometric method and the effectiveness of its application for determining the basic optical constants of crystals.

Analyzing the structure of the method under consideration, it is easy to see that, as a method of complete optical characterization, this method is undoubtedly the most important for crystals of monoclinic and triclinic systems. It is possible that in this case ellipsometry is the only effective method for determining the orientation of the optical indicatrix. Therefore, the results of studies of the $CdWO_4$ crystal (monoclinic system, class 2/*m*, space group of symmetry $P2/c$, $a$=0.502 nm, $b$=0.585 nm, $c$=0.507 nm, β=91.5º [13]) and steel, in our view, a decisive argument, which finally confirmed the effectiveness and prospects of using the ellipsometric method to determine the basic optical constants of any crystals. It should be said that all the $CdWO_4$ crystals studied by us were grown in the technological laboratory of the Department of Semiconductor Physics of the Ivan Franko National University of Lviv. In the articles devoted to studies of the optical properties of $CdWO_4$, there are very few data on the optical constants of this crystal. Thus, using the considered combined method, we, apparently, for the first time performed a complete optical characterization of the $CdWO_4$ crystal [3]. Table 2 shows the values of the principal refractive indices of the $CdWO_4$ crystal doped from the melt with a PbO impurity. For a thorough analysis of the accuracy of determining the optical constants, measurements were performed in two different configurations of pairs of planes at different angles of incidence of the laser beam on the crystal surface.

It is easy to see that in this case, as in the studies of the $LiNbO_3$ crystal (Table 1), the values of the principal refractive indices $n_g$, $n_m$ and $n_p$ decrease with an increase in the angle of incidence of the beam φ. In addition, the values of $n_g$, $n_m$ and $n_p$ obtained from the measurements in the two configurations are also slightly different. In our opinion, the most probable reason for such differences is the insufficiently precise determination of the orientation of the optical indicatrix. It is also obvious that the $n_p$ values differ significantly more than $n_g$ and $n_m$. In this case, the most probable reason for such differences is the structural features of $CdWO_4$. The $CdWO_4$ crystal cleaves very easily along the plane (010), which is the cleavage plane in this crystal. The positive thing is that in this way it is possible to obtain high-quality surfaces that do not have a layer damaged by mechanical and chemical processing (this is very important for ellipsometric measurements!). However, in this case, there is a possibility of the formation of a multilayer structure on the surface of the crystal due to delamination during cleavage. Since the refractive index $n_p$ characterizes the direction perpendicular to the plane (010), the effect of such a multilayer structure on the $n_p$ values obtained in different measurement configurations can be different.

If we average the values of the principal refractive indices according to the measurement data in two configurations of pairs of planes (i.e. the principal cross sections of the optical indicatrix), for example, at φ = 45 ° (Table 2), then with insignificant roundings we get:

$$N_g = 2.249(\pm 0.002) - i\cdot 0.0751(\pm 0.0002),$$
$$N_m = 2.185(\pm 0.002) - i\cdot 0.0628(\pm 0.0002),$$
$$N_p = 2.130(\pm 0.008) - i\cdot 0.0567(\pm 0.0007).$$

As we can see, the integral accuracy of determining the principal refractive indices from the results of measurements in various configurations at one angle of incidence is quite high (except for $N_p$, which is associated with the structural features of $CdWO_4$ and does not apply to other crystals).

Thus, if we consider only the real parts of the complex refractive indices (namely, $n_g$, $n_m$, $n_p$), then we can determine the value of birefringence, which is usually characterized by the maximum difference $\Delta n = n_g - n_p$ [14], and the angle between optical axes $2V$.

Table 2. The principal refractive indices of the $CdWO_4$ crystal (doped from the melt 0.375 wt.% PbO), determined from the results of measurements in two configurations (Fig. 2).

| Angle of incidence, φ | Principal refractive indices (wavelength λ = 632.8 nm) | | |
|---|---|---|---|
| | | Configuration of ellipsometric measurements | |
| | | $\boldsymbol{N_mX–N_pY–N_gZ}$<br>$\boldsymbol{N_mZ–N_pY–N_gX}$<br>$\boldsymbol{N_mY–N_pX–N_gZ}$ | $\boldsymbol{N_mX–N_pY–N_gZ}$<br>$\boldsymbol{N_mZ–N_pY–N_gX}$<br>$\boldsymbol{N_mZ–N_pX–N_gY}$ |
| 45° | $N_g=n_g–i\cdot k_g$ | 2.2505(±0.0008) – $i$·0.0749(±0.0002) | 2.2466(±0.0008) – $i$·0.0753(±0.0002) |
| | $N_m=n_m–i\cdot k_m$ | 2.1868(±0.0008) – $i$·0.0627(±0.0002) | 2.1832(±0.0008) – $i$·0.0630(±0.0002) |
| | $N_p=n_p–i\cdot k_p$ | 2.1374(±0.0008) – $i$·0.0560(±0.0002) | 2.1215(±0.0007) – $i$·0.0574(±0.0002) |
| 50° | $N_g=n_g–i\cdot k_g$ | 2.2441(±0.0007) – $i$·0.0727(±0.0002) | 2.2408(±0.0007) – $i$·0.0723(±0.0002) |
| | $N_m=n_m–i\cdot k_m$ | 2.1795(±0.0007) – $i$·0.0591(±0.0002) | 2.1764(±0.0006) – $i$·0.0587(±0.0002) |
| | $N_p=n_p–i\cdot k_p$ | 2.1276(±0.0006) – $i$·0.0604(±0.0002) | 2.1140(±0.0006) – $i$·0.0577(±0.0002) |
| 55° | $N_g=n_g–i\cdot k_g$ | 2,2409(±0.0006) – $i$·0.0742(±0.0001) | 2.2382(±0.0006) – $i$·0.0734(±0.0001) |
| | $N_m=n_m–i\cdot k_m$ | 2.1784(±0.0006) – $i$·0.0562(±0.0001) | 2.1757(±0,0006) – $i$·0.0554(±0,0001) |
| | $N_p=n_p–i\cdot k_p$ | 2.1203(±0,0005) – $i$·0.0636(±0,0001) | 2.1090(±0.0006) – $i$·0.0596(±0.0001) |
| 60° | $N_g=n_g–i\cdot k_g$ | 2.2409(±0,0005) – $i$·0.0813(±0,0001) | 2,2383(±0.0006) – $i$·0.0806(±0.0001) |
| | $N_m=n_m–i\cdot k_m$ | 2.1747(±0,0005) – $i$·0.0576(±0,0001) | 2,1723(±0.0006) – $i$·0.0570(±0.0001) |
| | $N_p=n_p–i\cdot k_p$ | 2.1142(±0.0005) – $i$·0.0677(±0.0001) | 2.1039(±0.0006) – $i$·0.0644(±0.0001) |

We recall that in optically biaxial crystals, both optical axes always lie in the principal cross section $\boldsymbol{N_gON_p}$ of the optical indicatrix (see Fig. 8 [1]). Usually, the angle $2V$ is determined, the bisector of which is the axis $\boldsymbol{N_g}$ of the optical indicatrix. The angle $V$ between the axis $\boldsymbol{N_g}$ of the optical indicatrix and the optical axis of the crystal was determined by the formula [14]:

$$tgV = \sqrt{\frac{n_p^{-2} - n_m^{-2}}{n_m^{-2} - n_g^{-2}}}\,. \tag{9}$$

The results of calculations of $\Delta n$ and $2V$ are given in Tables 3 and 4. The same tables also indicate the optical sign of the $CdWO_4$ crystal, determined both in accordance with the criterion ($n_g - n_m < > n_m - n_p$), and by the value of the angle $2V$ [14].

Table 3. The values of birefringence $\Delta n$ and the optical sign of the $CdWO_4$ crystal (0.375 wt.% PbO) for two configurations of measurements performed at different angles of incidence of the laser beam.

| Angle of incidence, φ | Birefringence values, $\Delta n = n_g - n_p$ (wavelength λ = 632.8 nm) | | | |
|---|---|---|---|---|
| | Configuration of ellipsometric measurements<br>$N_mX$–$N_pY$–$N_gZ$<br>$N_mZ$–$N_pY$–$N_gX$<br>$N_mY$–$N_pX$–$N_gZ$ | Optical sign of the crystal, ($n_g - n_m < > n_m - n_p$) | Configuration of ellipsometric measurements<br>$N_mX$–$N_pY$–$N_gZ$<br>$N_mZ$–$N_pY$–$N_gX$<br>$N_mZ$–$N_pX$–$N_gY$ | Optical sign of the crystal, ($n_g - n_m < > n_m - n_p$) |
| 45° | 0.1130(±0.0005) | + | 0.1251(±0.0005) | + |
| 50° | 0.1165(±0.0005) | + | 0.1268(±0.0005) | + |
| 55° | 0.1206(±0.0005) | + | 0.1291(±0.0005) | - |
| 60° | 0.1267(±0.0005) | + | 0.1344(±0.0005) | - |

Table 4. The angle between the optical axes and the optical sign of the $CdWO_4$ crystal (0.375 wt.% PbO) for two configurations of measurements performed at different angles of incidence of the laser beam.

| Angle of incidence, φ | Angle between optical axes, $2V$ (wavelength λ = 632.8 nm), (bisector of angle – axis $N_g$ of optical indicatrix) | | | |
|---|---|---|---|---|
| | Configuration of ellipsometric measurements<br>$N_mX$–$N_pY$–$N_gZ$<br>$N_mZ$–$N_pY$–$N_gX$<br>$N_mY$–$N_pX$–$N_gZ$ | Optical sign of the crystal (by angle $2V$) | Configuration of ellipsometric measurements<br>$N_mX$–$N_pY$–$N_gZ$<br>$N_mZ$–$N_pY$–$N_gX$<br>$N_mZ$–$N_pX$–$N_gY$ | Optical sign of the crystal (by angle $2V$) |
| 45° | 85°0′(±20′) | + | 91°40′(±20′) | - |
| 50° | 86°0′(±20′) | + | 91°35′(±20′) | - |
| 55° | 90°20′(±20′) | - | 94°25′(±20′) | - |
| 60° | 89°55′(±20′) | + / - | 93°40′(±20′) | - |

Based on the results obtained (Tables 3 and 4), it can be concluded that $CdWO_4$ doped with PbO impurity is a pronounced biaxial crystal with an angle between the optical axes close to 90°. However, a rather large difference in the values of the principal refractive indices obtained from the results of measurements in two configurations of pairs of planes does not allow one to confidently determine the optical sign of the $CdWO_4$ crystal. As you can see from the table 3 and 4, there is no unambiguity in the results of determining the optical sign both in accordance with the ($n_g - n_m <> n_m - n_p$) criterion, and in the value of the angle $2V$. In our opinion, this fact does not diminish the efficiency of using the combined ellipsometric method for optical characterization of crystals, but only emphasizes the importance of high-quality preparation of research objects. This will make it possible to achieve the maximum correspondence of the crystals under study to the theoretical models that are used for the analysis of measurements.

One more important circumstance should be noted. Despite their, so to speak, “imaginary” status, the extinction coefficients $k_g$, $k_m$, $k_p$ ($k_o$, $k_e$) have a very real physical meaning. In the case of weakly absorbing substances (and $CdWO_4$ and $LiNbO_3$ at a wavelength of $\lambda$ = 632.8 nm are just such substances), the extinction coefficients characterize the intensity of light scattering by a crystal. Obviously, the values of the extinction coefficients $k_g$, $k_m$, $k_p$ ($k_o$, $k_e$) determine both the quality of the investigated surface and the structural features (in particular, the structure of defects) of the crystal. At sufficiently high values of the extinction coefficients ($k > 0.2$), significant light scattering can cause significant errors in determining the optical constants of a crystal.

## 4. Conclusions

Thus, the results of testing the second stage of the combined elliptical method allow us to draw the following conclusions. First, the proposed method is quite correct and applicable for crystals of any crystallographic system. Second, the accuracy of determining the optical constants of crystals by this method is sufficiently high even from the results of measurements in different measuring configurations and at several angles of incidence (integral accuracy). This accuracy can be increased by determining the orientation of the optical indicatrix in the crystal with the highest possible accuracy. In the next part of this article, we plan to present a technique for accurately determining the orientation of optical axes in crystals, which is the third stage of the considered combined ellipsometric method. This technique also makes it possible to refine the orientation of the optical indicatrix in the crystal.

## REFERENCES

[1] *Belyukh V., Pavlyk B.* The combined ellipsometric method of complete optical characterization of crystals. I. Determination of the orientation of the optical indicatrix. // Electronics and information technologies. – 2021. – Issue 15. – P. 112-123. https://doi.org/10.30970/eli.15.11

[2] *Graves R. H. W.* Determination of the optical constants of anisotropic crystals // Journal of the Optical Society of America. – 1969. – Vol. 59, No. 9. – P. 1225-1228. https://doi.org/10.1364/JOSA.59.001225

[3] *Belyukh V., Pashkowsky M.* Combined ellipsometric technique of the optical characterization of crystals. Part I. // Visnyk of the Lviv University. Series Physics – 2010. – Issue 45. – P. 55-69. [In Ukrainian]

[4] *Prokhorov A. M., Kuzminov Yu. S.* Physics and Chemistry of Crystalline Lithium Niobate. – The Adam Hilger Series on Optics and Optoelectronics, Bristol and New York. – 1990. – 337 p.

[5] *Kuzminov Yu. S.* Electro-optical and nonlinear-optical crystal of lithium niobate. – Moscow:

Nauka (Publishing House), 1987. – 264 p. [In Russian]

[6] *Blistanov A. A, Bondarenko V. S., Perelomova N. V., Strizhevskaya F. N., Tchkalova V. V., Shaskolskaya M. P.* Acoustic Crystals: A Handbook (*ed.* M.P. Shaskolskaya). – Moscow: Nauka (Publishing House), 1982. – 632 p. [In Russian]

[7] *Boyd G. D., Miller R. C., Nassau K., Bond W. L. and Savage A.* $LiNbO_3$: An efficient phase machable nonlinear optical material// Applied Physics Letters. – 1964. – Vol. 5, №11. – P. 234-236. https://doi.org/10.1063/1.1723604

[8] *Midwinter J. E.* Lithium Niobate: Effects of Composition on the Refractive Indices and Optical Second Harmonic Generation // Journal of Applied Physics. – 1968. – Vol. 39, №7. – P. 3033-3038. https://doi.org/10.1063/1.1656727

[9] *Nelson D. F., Mikulyak R. M.* Refractive indices of congruently melting lithium niobate // Journal of Applied Physics. – 1974. – Vol. 45, №8. – P. 3688-3689. https://doi.org/10.1063/1.1663839

[10] *Shlarb U., Betzler K.* Refractive indices of lithium niobate as a function of temperature, wavelength and composition: a generalized fit // Phys. Rev. B. – 1993. – Vol. 48, №21. – P. 15613-15620. https://doi.org/10.1103/PhysRevB.48.15613

[11] *Shlarb U., Betzler K.* Influence of the defect structure on the refractive indices of undoped and Mg-doped lithium niobate // Phys. Rev. B. – 1994. – Vol. 50, №2. – P. 751-757. https://doi.org/10.1103/PhysRevB.50.751

[12] *Shlarb U., Betzler K.* Refractive indices of lithium niobate as a function of wavelength and composition // Journal of Applied Physics. – 1993. – Vol. 73, №7. – P.3472-3476. https://doi.org/10.1063/1.352951

[13] *Chychagov A.P., Ilyukhin V. V., Belov N. V.* Crystal structure of cadmium tungstate $CdWO_4$ // Dokl. Akad. Nauk (SSSR). – 1966. – Vol. 166, No. 1. – P. 87-89 (English transl.: Sov. Phys. Dokl. – 1966. – Vol. 11. – P. 11-13).
http://mi.mathnet.ru/rus/dan/v166/i1/p87

[14] *Sirotin Yu.I., Shaskolskaya M.P.* Fundamentals of crystal physics. – Moscow: Nauka (Publishing House), 1979. – 640 p. [In Russian]

## КОМБІНОВАНА ЕЛІПСОМЕТРИЧНА МЕТОДИКА ПОВНОЇ ОПТИЧНОЇ ХАРАКТЕРИЗАЦІЇ КРИСТАЛІВ. II. ВИЗНАЧЕННЯ ОПТИЧНИХ КОНСТАНТ КРИСТАЛА

**В. Белюх, Б. Павлик**

*Львівський національний університет імені Івана Франка,*
*вул. Ген. Тарнавського, 107, 79017 Львів, Україна*
*belyukh@electronics.lnu.edu.ua*

У цій частині праці описаний другий етап комбінованої еліпсометричної методики повної оптичної характеризації кристалів. Даний етап складається з таких частин: а) приготування якісних площин кристала, які відповідають головним перерізам оптичної індикатриси; б) виконання необхідної кількості еліпсометричних вимірювань на цих площинах; в) визначення головних показників заломлення кристала шляхом розв’язку відповідної системи рівнянь. Тестування другого етапу комбінованої еліпсометричної методики було виконане на кристалах ніобату літію ($LiNbO_3$) і вольфрамату кадмію ($CdWO_4$). Одержані результати вимірювань оптично одновісного кристала $LiNbO_3$ цілком підтвердили коректність пропонованої методики та її придатність для повної оптичної характеризації кристалів. Зокрема, значення головних показників заломлення $\{n_o = 2.280(\pm0.003)$, $n_e = 2.202(\pm0.002)\}$ і подвійного променезаломлення $\{\Delta n = -0.0775(\pm0.0015)\}$ кристала $LiNbO_3$ добре узгоджуються зі значеннями $n_o$, $n_e$, $\Delta n$, одержаними іншими дослідниками іншими методами. З точки зору ефективності застосування, пропонований метод є найбільш важливим для кристалів моноклінної і триклінної сингоній. Тому дослідження оптично двовісного кристала $CdWO_4$ (моноклінна сингонія) були дуже важливими для аналізу точності визначення оптичних констант. Для загальності такого аналізу вимірювання були виконані у різних вимірювальних конфігураціях за декількох кутів падіння лазерного променя. Мета таких вимірювань: оцінити інтегральну точність визначення оптичних констант кристала. Зокрема, за результатами вимірювань у двох конфігураціях (кут падіння 45°) одержані такі значення головних показників заломлення кристала $CdWO_4$ (легований з розплаву 0.375 мас.% PbO): $n_g = 2.249\pm0.002$, $n_m = 2.185\pm0.002$, $n_p = 2.130\pm0.008$. За значеннями $n_g$, $n_m$ і $n_p$ були визначені кут між оптичними осями і оптичний знак кристала. Експериментально доведено, що кристала $CdWO_4$ є яскраво вираженим двовісним кристалом з кутом між оптичними осями близьким до 90°. Проаналізовані можливі шляхи покращення точності визначення оптичних констант кристалів.

*Ключові слова*: еліпсометрія, оптична індикатриса, головні показники заломлення, одновісні і двовісні кристали.

*Стаття: надійшла до редакції 10.11.2021,*
*доопрацьована 15.11.2021,*
*прийнята до друку 20.11.2021*