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 PHYSICAL PROPERTIES OF CRYSTALS
 

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# ACCOUNTING FOR THE IMPERFECTION OF THE SPECTROPHOTOMETRIC COMPLEX OPTICAL ELEMENTS WHEN MEASURING TRANSMISSION SPECTRA OF GYROTROPIC UNIAXIAL CRYSTALS. I. SAMPLES ARE CUT PERPENDICULAR TO THE OPTICAL AXIS

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Received November 07, 2024

Revised November 07, 2024

Accepted November 26, 2024

**Abstract.** A theoretical and experimental study of the effect of imperfections of the polarizer, analyzer and photomultiplier tube (PMT) on the measurement results of spectral transmission dependences of catangasite crystals  $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$  cut perpendicular to the optical axis has been carried out. There is a difference between the spectra obtained with *p*- and *s*-polarizations of incident light and the jumps on the curves at  $\lambda = 1050$  nm. This is due to the imperfection of the PMT and the optical activity of the crystal. The estimation of the parameters of the PMT from experimental data depending on the wavelength is carried out. The influence of the imperfection of the PMT and polarizers on the results of calculating the rotation of the plane of polarization of light  $\rho$  is studied. It is shown that transmission spectra measured at angles between the polarizer and the analyzer  $\pm 45^\circ$  are necessary for accurate calculation of the value of  $\rho$ . The measurement errors obtained depend on the change of optical elements in a particular device.

DOI: 10.31857/S00234761250106e3

## INTRODUCTION

To correctly interpret the results of spectrophotometric measurements, it is necessary to take into account the errors associated with the imperfection of the optical elements of the device [1]. It is also necessary to take into account the errors associated with the imperfection of the sample: defects, inhomogeneities, quality of surface polishing, orientation accuracy. In addition, there is an error in the installation of the sample in the measuring chamber relative to the incident beam.

Thus, in real experiments, the error of spectrophotometric measurements exceeds that specified in the operating manual. The problem of imperfection of individual optical elements of the device is not discussed so often, but it can significantly affect the results of measurements of optical properties.

In [2], the influence of imperfections of the elements of a spectrophotometric complex on the transmission coefficients of light passing through a plate of a uniaxial optically active crystal cut perpendicular to the optical axis was theoretically studied. However, this work does not contain enough experimental data, and not all interesting cases were considered.

Each device has its own characteristics that determine the errors of the measurements. To estimate these errors, it is necessary to measure the spectral dependences of the light transmission coefficients in unpolarized and polarized light for different samples at different orientations. In this case, it is better to use crystals whose optical properties have been studied well enough. An example of such crystals are crystals of the langasite family, which were first grown by B.V. Mill [3]. The first measurements of the refractive indices and optical activity parameters of langasite are presented in [4, 5]. At present, these crystals are widely used in practice and are grown in good optical quality [6, 7].

This work is devoted to theoretical and experimental study of imperfection of optical elements of spectrophotometer on the example of measurements of crystals of catangasite  $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$ , cut perpendicular to the optical axis. Analysis of influence of imperfection of polarizer, analyzer and photomultiplier tube (PMT) on measured spectra of transmission coefficients is carried out.

If we take other crystals and another spectrophotometer, errors may appear that differ from those studied in this work. But with the help of the

obtained results, it is possible to determine what values need to pay attention to in order to obtain correct results for different crystals and on any spectrophotometer.

# MEASUREMENT AND CALCULATION OF LIGHT TRANSMISSION COEFFICIENTS TAKING INTO ACCOUNT THE NON-IDEALITY OF THE ELEMENTS OF THE SPECTROPHOTOMETRIC COMPLEX

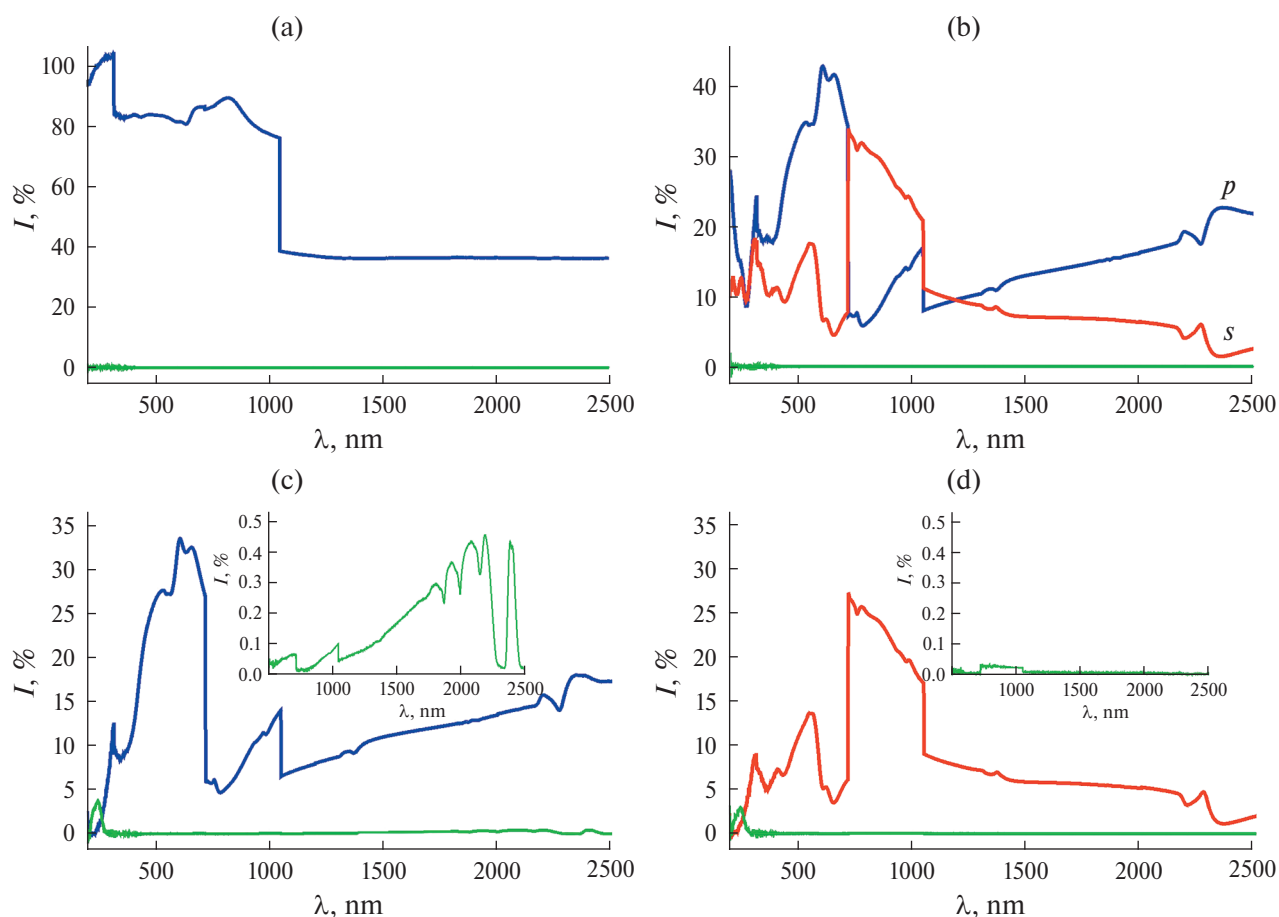
Measurements of the transmission spectra of the crystals were carried out in the range  $\lambda = 200\text{--}2500$  nm with a step of 1 nm on a Cary-5000 spectrophotometer with a universal measurement accessory UMA [8] in unpolarized and polarized light using two Glan–Taylor polarizers.

Let us consider three cases of measuring the light transmission spectra: without a polarizer; with one polarizer in positions that correspond to the *p*- and *s*-polarizations of the light incident on the crystal; with a polarizer and analyzer at different angles  $\tau$  between the directions of their greatest transmission. The crystals

studied are transparent in most of the selected range, without clearly defined absorption bands.

The measured intensities of transmitted light are normalized based on the condition that the transmission without a sample is 100%. Baselines were used to normalize the transmission spectra.

The baselines for the three cases considered are shown in Fig. 1. The baseline corresponding to 100% transmission without a polarizer (Fig. 1a) has a noticeable jump at 1050 nm, probably associated with a change in the channel in the device's detector (transition from Si to InGaAs in accordance with the standard settings of the Cary-5000 spectrophotometer with the UMA accessory [9]). There is also an insignificant "step" at  $\lambda = 720$  nm (at this wavelength, a "grating change" occurs [9]). Based on the appearance of the baselines with a polarizer (Fig. 1b), it can be assumed that the polarization of the incident light changes abruptly at wavelengths of  $\lambda = 720$  and 1050 nm, since there are breaks in the curves at these wavelengths. When measuring with a polarizer and analyzer, the accuracy of the zero baseline is important, i.e. the difference in transmission of crossed



**Fig. 1.** Baselines: a – without polarizer, 100 and 0%; b – 100 and 0% with polarizer for *s*- and *p*-polarizations; c, d – with polarizer and analyzer, 100% – polarizer and analyzer are parallel, 0% – polarizer and analyzer are crossed, the insets show the zero line on an enlarged scale; c – *p*-polarization, d – *s*-polarization.

polarizers from zero should be minimal (Fig. 1c, 1d). In the UV region at  $\lambda = 200\text{--}300\text{ nm}$ , measurements with these polarizers are impossible (the transmission of crossed polarizers becomes greater than their transmission in the parallel position). If the position of parallel polarizers corresponds to  $p$ -polarization, the transmission of polarizers in the visible region is greater (Fig. 1c), therefore, it is better to use this position for measurements in the visible region. In the IR region, on the contrary, it is better to carry out measurements with  $s$ -polarization, since the transmission of crossed polarizers is noticeably less than with  $p$ -polarization (inserts in Fig. 1c, 1d).

All baselines (Fig. 1) have features at wavelengths  $\lambda = 720$  and  $1050\text{ nm}$ . Let us consider how these features will affect the measurements of light transmission spectra.

To calculate the intensity of transmitted light, the Mueller matrix method can be used [1]. We calculate the intensity of light as the first component of the Stokes

vector  $S$ . In the case of the presence of both a polarizer and an analyzer, the vector  $S$  has the form:

$$S = M_F \cdot M_A \cdot M \cdot M_P \cdot S_0, \quad (1)$$

where  $M_P$ ,  $M_A$ ,  $M$ ,  $M_F$  are the Mueller matrices of the polarizer, analyzer, plate and PMT, respectively,  $S_0$  is the Stokes vector of incident light; for unpolarized light  $S_0 = \{1, 0, 0, 0\}$ . We normalize the calculated spectra in the same way as experimental spectra should be normalized – based on the condition that the transmission of the elements under consideration without a sample is 100%. All calculations were performed using the Wolfram Mathematica program [10].

The Mueller matrix of a uniaxial absorbing optically active crystal in the system of principal axes (the projection of the optical axis onto the plane of the plate is parallel to the  $x$  axis) has the form [11]:

$$M = e^{-\zeta} \begin{pmatrix} \text{ch}\delta & \cos 2\gamma \text{sh}\delta & 0 & \sin 2\gamma \text{sh}\delta \\ \cos 2\gamma \text{sh}\delta & \cos\Delta + \cos^2 2\gamma (\text{ch}\delta - \cos\Delta) & -\sin 2\gamma \sin\Delta & \sin 2\gamma \cos 2\gamma (\text{ch}\delta - \cos\Delta) \\ 0 & \sin 2\gamma \sin\Delta & \cos\Delta & -\cos 2\gamma \sin\Delta \\ \sin 2\gamma \text{sh}\delta & \sin 2\gamma \cos 2\gamma (\text{ch}\delta - \cos\Delta) & \cos 2\gamma \sin\Delta & \cos\Delta + \sin^2 2\gamma (\text{ch}\delta - \cos\Delta) \end{pmatrix}, \quad (2)$$

$\Delta = 2\pi d(n_2 - n_1)/\lambda$  is the phase difference in the plate,  $\zeta = 2\pi d(\kappa_1 + \kappa_2)/\lambda$ , the value  $\delta = 2\pi d(\kappa_2 - \kappa_1)/\lambda$  characterizes the dichroism of the plate,  $n_1$ ,  $n_2$  are the refractive indices,  $\kappa_1$ ,  $\kappa_2$  are the absorption indices of the crystal in a given direction,  $\cos 2\gamma = \frac{1-k^2}{1+k^2}$ ,  $\sin 2\gamma = \frac{2k}{1+k^2}$ ,  $k = \text{tg}\gamma$ ,  $k = \text{tg}\gamma$  is the ellipticity of eigenwaves [12].

In the case of a sample cut perpendicular to the optical axis, linear birefringence and linear dichroism are zero. In an optically active crystal, two circularly polarized waves propagate along the optical axis. In this case,  $k = \pm 1$ ,  $\Delta = 2\rho d$ ,  $\rho$  is the rotation of the plane of polarization of light passing through the crystal [13],  $\delta$  characterizes circular dichroism – the difference in the absorption of waves of

right and left circular polarizations [14]. For the Mueller matrix, we obtain (the optical axis is parallel to the  $z$  axis):

$$M = e^{-\zeta} \begin{pmatrix} \text{ch}\delta & 0 & 0 & \text{sh}\delta \\ 0 & \cos 2\rho d & -\sin 2\rho d & 0 \\ 0 & \sin 2\rho d & \cos 2\rho d & 0 \\ \text{sh}\delta & 0 & 0 & \text{ch}\delta \end{pmatrix}. \quad (3)$$

The optical elements in the case under consideration include a polarizer, an analyzer, and a PMT. All of them may be non-ideal. Let  $p_1$  be the polarizer transmission in the direction of greatest transmission, and  $p_2$  be the polarizer transmission in the perpendicular direction [1]. In the ideal case,  $p_2 = 0$ . The matrix of a non-ideal polarizer has the form [1]:

$$M_P = \frac{1}{2} \begin{pmatrix} p_1 + p_2 & (p_1 - p_2)\cos 2\alpha & (p_1 - p_2)\sin 2\alpha & 0 \\ (p_1 - p_2)\cos 2\alpha & (p_1 + p_2)\cos^2 2\alpha + 2\sqrt{p_1 p_2} \sin^2 2\alpha & (p_1 + p_2 - 2\sqrt{p_1 p_2})\sin 2\alpha \cos 2\alpha & 0 \\ (p_1 - p_2)\sin 2\alpha & (p_1 + p_2 - 2\sqrt{p_1 p_2})\sin 2\alpha \cos 2\alpha & (p_1 + p_2)\sin^2 2\alpha + 2\sqrt{p_1 p_2} \cos^2 2\alpha & 0 \\ 0 & 0 & 0 & 2\sqrt{p_1 p_2} \end{pmatrix}. \quad (4)$$

Here,  $\alpha$  is the angle between the direction of greatest transmission of the polarizer and the  $x$ -axis. The direction  $x$  is chosen so that  $\alpha = 0$  corresponds to the

$p$ -polarization of the light passing through the polarizer,  $\alpha = 90^\circ$  –  $s$ -polarization. A similar matrix can be written for the analyzer.

The non-ideality of the polarizer can be estimated by the transmission of crossed polarizers (the ratio of the transmission of crossed and parallel polarizers is  $\sim 2p_2/p_1$ ). From Fig. 1c, 1d it is evident that the value of  $p_2$  is significant in the range of  $\lambda = 200\text{--}300\text{ nm}$ . Also,  $p_2 \neq 0$  in the IR region with p-polarization (Fig. 1c), but in this case the ratio  $p_2/p_1$  does not exceed 0.015.

In addition to the polarizer and analyzer, the error may be introduced by the detector of the device (PMT). Let the parameter  $f_1$  characterize the registration of p-polarized radiation,  $f_2$  – the registration of s-polarized radiation. The Mueller matrix of a non-ideal PMT has the same form as the matrix of a non-ideal polarizer [15]. In the ideal case  $f_1 = f_2 = 1$ , the Mueller matrix of the PMT becomes a unit matrix, and the obtained light intensity coincides with the intensity without taking the PMT into account. In the case of  $f_1 \neq f_2$ , the PMT plays the role of a “partial” analyzer.

Calculation by the Mueller matrix method for uniaxial crystals cut perpendicular to the optical axis is considered for some cases in [2]. In this case, the non-ideality of optical elements is considered in [2] without assessing the corresponding parameters for a specific device. In this paper, we will compare experimental and calculated data for specific crystals of practical interest.

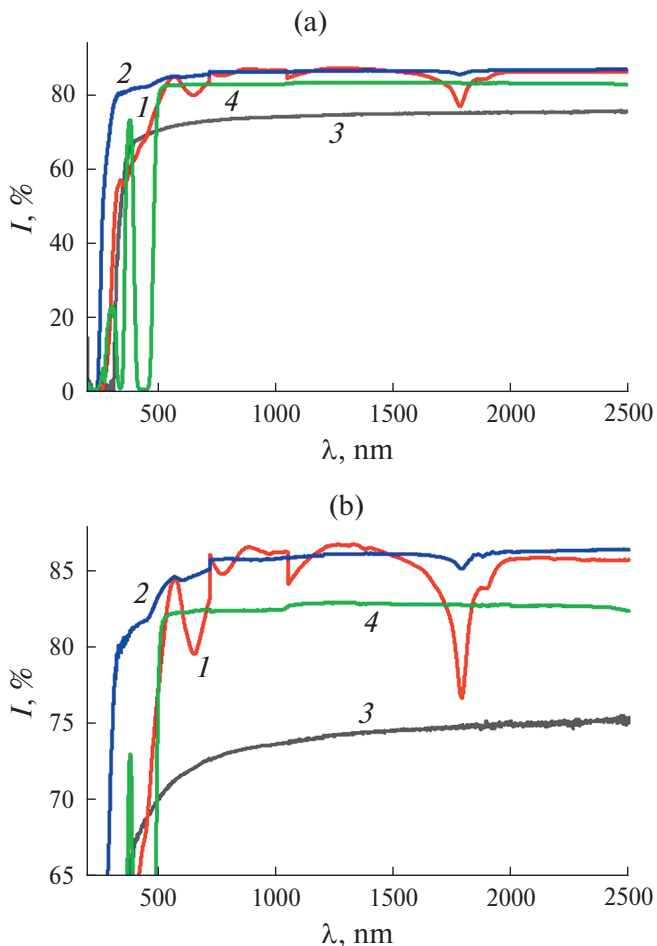
#### TRANSMISSION SPECTRA OF A PLATE CUT PERPENDICULAR TO THE OPTICAL AXIS (Z-CUT)

##### *Without polarizer*

Let us consider the transmission spectra of catangasite  $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$  crystals (thick sample  $d = 10\text{ mm}$  and thin sample  $d = 1\text{ mm}$ ), lithium niobate  $\text{LiNbO}_3$  and garnet  $\text{Gd}_3\text{Al}_2\text{Ga}_3\text{O}_{12}:\text{Ce}$  in unpolarized light (Fig. 2). All samples were cut from crystals grown at OJSC “Fomos Materials” [6]. The spectrum for the thick sample  $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$  has clearly defined jumps at  $\lambda = 720\text{ nm}$  (“grating change”) and  $1050\text{ nm}$  (channel change in the device detector). For the thin sample  $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$ , the jump is noticeable only at  $\lambda = 720\text{ nm}$ . At the same time, the jumps for  $\text{LiNbO}_3$  and  $\text{Gd}_3\text{Al}_2\text{Ga}_3\text{O}_{12}:\text{Ce}$  are practically unnoticeable.

For both samples of  $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$  there is an absorption band at  $\lambda = 1800\text{ nm}$ . Note that this band is present in different langasites, its nature has not yet been determined unambiguously.

For unpolarized light  $S_0 = \{1, 0, 0, 0\}$ ,  $I = I_0 e^{-\zeta}$ . Thus, if we assume that unpolarized light is incident, there should be no jumps in the graphs.



**Fig. 2.** Transmission spectra at different scales: 1 – thick sample of catangasite  $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$  ( $d = 10\text{ mm}$ ), 2 – thin sample of  $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$  ( $d = 1\text{ mm}$ ), 3 – lithium niobate  $\text{LiNbO}_3$  ( $d = 1\text{ mm}$ ), 4 – garnet  $\text{Gd}_3\text{Al}_2\text{Ga}_3\text{O}_{12}:\text{Ce}$  ( $d = 1.94\text{ mm}$ ).

Since the incident light is not actually unpolarized, but has a partial elliptical polarization, the jump at  $\lambda = 720\text{ nm}$  can be associated with a change in the polarization of the incident light. Let us calculate the intensity of the transmitted light for the case of incident light of arbitrary elliptical polarization.

If we write the Stokes vector of incident radiation of elliptical polarization in the form [1]:

$$S_0 = \{1, \cos 2\omega \cos 2\chi, \cos 2\omega \sin 2\chi, \sin 2\omega\}, \quad (5)$$

where  $\chi$  characterizes the azimuth, and  $\omega$  is the ellipticity of the incident light, from (1) we obtain:

$$I = I_0 e^{-\zeta} \frac{(f_1 + f_2) \text{ch} \delta + (f_1 - f_2) \cos 2\omega \cos [2(\rho d + \chi)] + (f_1 + f_2) \sin 2\omega \text{sh} \delta}{f_1 + f_2 + (f_1 - f_2) \cos 2\omega \cos 2\chi}. \quad (6)$$

At  $\lambda = 720$  nm, a “lattice change” occurs and the polarization of the incident light may change abruptly. At  $\lambda = 1050$  nm, as a result of a change in the parameters of the device's detector, the values of  $f_1$  and  $f_2$  may change abruptly. This causes a shift in the dependences of the transmission coefficients (jumps in the curves, Fig. 2). In the case of an ideal PMT,  $f_1 = f_2$ , and the intensity of the transmitted light does not depend on the polarization of the incident light. With a non-ideal PMT, there is a dependence on the polarization of the incident light, since expression (6) contains the parameters  $\omega$  and  $\chi$ , but in the absence of optical activity, these parameters should be reduced during normalization. This is confirmed by the absence of noticeable shifts in the curves for optically inactive  $\text{LiNbO}_3$  and  $\text{Gd}_3\text{Al}_2\text{Ga}_3\text{O}_{12}:\text{Ce}$  crystals, as well as by the fact that for a thick  $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$  sample with a larger  $\rho d$  value, these shifts are much more pronounced than for a thin one.

Note that jumps in the transmission spectra appear for any crystals, including optically inactive ones (Fig. 2, curves 3, 4), but in the absence of optical activity they are small and less than the experimental error. Therefore, we can conclude that in this case there are other errors.

For a more accurate assessment of experimental errors, let us consider the transmission spectra in polarized light.

*With polarizer without analyzer,  
p- and s-polarization of incident light*

The transmitted light intensities obtained for  $p$ - and  $s$ -polarizations of incident light for glass samples and catangasite crystals  $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$  of different thicknesses are shown in Fig. 3. Note that, in the ideal case, the transmitted light intensity should be the same for  $p$ - and  $s$ -polarization.

The observed difference in intensities may be due to the imperfection of the optical elements: the polarizer and the photomultiplier. Then, in the case of incidence of elliptical polarized light, if the polarizer is oriented in the  $x$  direction ( $p$ -polarized light falls on the crystal):

$$\begin{aligned} I_p = I_{0p} e^{-\zeta} & ((f_1 + f_2)(p_1 + p_2) \text{ch} \delta + \\ & + (f_1 - f_2) \cos \Delta (p_1 - p_2 + (p_1 + p_2) \cos 2\omega \cos 2\chi) + \\ & + \cos 2\omega ((f_1 + f_2)(p_1 - p_2) \cos 2\chi \text{ch} \delta - \\ & - 2(f_1 - f_2) \sqrt{p_1 p_2} \sin \Delta \sin 2\chi) + \\ & + 2(f_1 + f_2) \sqrt{p_1 p_2} \sin 2\omega \text{sh} \delta) / (2(f_1 p_1 + f_2 p_2 + \\ & + (f_1 p_1 - f_2 p_2) \cos 2\omega \cos 2\chi)). \end{aligned} \quad (7)$$

With an ideal PMT ( $f_1 = f_2$ ), but an imperfect polarizer, we obtain:

$$I_p = I_{0p} e^{-\zeta} \left( \text{ch} \delta + \frac{2\sqrt{p_1 p_2} \sin 2\omega \text{sh} \delta}{p_1 + p_2 + (p_1 - p_2) \cos 2\omega \cos 2\chi} \right). \quad (8)$$

The additive associated with the non-ideality of the polarizer is proportional to the product of small values of  $\text{sh} \delta$  and  $p_2^{(1/2)}$ ; in the absence of circular dichroism ( $\delta = 0$ ), the values of  $p_1$  and  $p_2$  are reduced during normalization. Therefore, since we only take into account first-order errors, the non-ideality of the polarizer can be ignored in this case.

If we consider the polarizer to be ideal ( $p_2 = 0$ ), the formulas are significantly simplified. For  $p$ - and  $s$ -polarizations we obtain:

$$I_p = \frac{I_{0p}}{2} e^{-\zeta} ((1 + f_2 / f_1) \text{ch} \delta + (1 - f_2 / f_1) \cos(2\rho d)), \quad (9)$$

$$I_s = \frac{I_{0s}}{2} e^{-\zeta} ((1 + f_1 / f_2) \text{ch} \delta + (1 - f_1 / f_2) \cos(2\rho d)). \quad (10)$$

In this case, these formulas have the same form when unpolarized light and light of arbitrary elliptical polarization fall on the polarizer. It is evident that in the case of a non-ideal PMT ( $f_2 \neq f_1$ ), the intensity of the transmitted light depends on the value of optical activity. In the ideal case,  $I_{0p} = I_{0s}$  should be, but this is not the case in Fig. 3. This difference is most likely due to the normalization of the device ( $p$ - and  $s$ -polarizations are normalized differently). In this case, different values of  $I_p$  and  $I_s$  are observed, including for glass that does not have optical activity and birefringence (curves 1 in Fig. 3a). For a thick sample of  $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$ , a noticeable jump is observed in the curves at  $\lambda = 1050$  nm, associated with a change in the parameters of the photomultiplier (the ratio  $f_1/f_2$ ). From (9), (10) it is evident that the jump will be the largest at  $\cos 2\rho d = -1$ , and at  $\cos 2\rho d = 1$  it is absent (if we assume  $\delta = 0$ ). Using the values of  $\rho$  from [7, 16], for a thick sample of  $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$  we obtain  $\cos 2\rho d = -0.91$ , and for a thin sample  $\cos 2\rho d = 0.94$ . Therefore, for a thin sample of  $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$  the jump is practically not noticeable. Also, for the thick sample there are oscillations at wavelengths  $\lambda < 1050$  nm (Fig. 3b), associated with a large value of  $\rho d$  in this region. At  $\lambda = 720$  nm there is no jump on any of the curves.

Thus, individual spectra  $I_p$  and  $I_s$  become different due to different normalization for  $p$ - and  $s$ -polarizations and non-ideality of the PMT. The difference between the obtained curves and their intersection points depend primarily on the optical activity and the value of  $f_1/f_2$ .

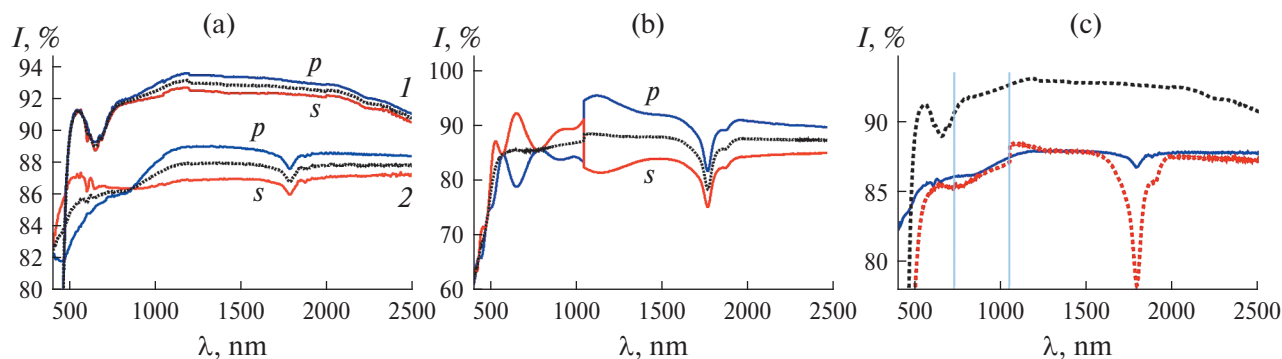
To obtain a more correct spectrum, we consider the value  $(I_p + I_s)/2$  (Fig. 3a, 3b, dotted curves). Circular dichroism in this case is very small, so we assume  $\delta = 0$ . Let  $f_2/f_1 = 1 + h$ ,  $|h| \ll 1$ . Then, in the first approximation,  $f_1/f_2 \approx 1 - h$ ,

$$I_p = (I_{0p}/2) e^{-\zeta} (2 + h - h \cos 2\rho d),$$

$$I_s = (I_{0s}/2) e^{-\zeta} (2 - h + h \cos 2\rho d).$$

Considering  $I_{0s} = I_{0p} + \Delta I$ ,  $\Delta I \ll I_{0s}$ ,  $\Delta I \ll I_{0p}$  and taking into account only the terms of the first order of smallness, we obtain:





**Fig. 3.** Results of measuring the intensity of transmitted light for p- and s-polarizations and averaged spectra  $(I_p + I_s)/2$ : a – control light filter made of Zhs-3 glass,  $d = 2.14$  mm (1), and  $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$ ,  $d = 1$  mm (2); b –  $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$ ,  $d = 10$  mm; c – comparison of averaged spectra for glass (1), thin (2) and thick (3)  $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$  samples.

$$(I_p + I_s)/2 = e^{-\xi}(I_{0p} + \Delta I/2). \quad (11)$$

Thus, the value of  $(I_p + I_s)/2$  in the first approximation does not depend on the values of optical activity and  $f_2/f_1$ . Therefore, the half-sum  $(I_p + I_s)/2$  more correctly determines the transmission of the crystal than individual spectra of  $I_p$  and  $I_s$ . For a thick sample of katangasite ( $d = 10$  mm), the use of the averaged spectrum does not completely eliminate the errors associated with the non-ideality of the PMT (a jump remains at  $\lambda = 1050$  nm, Fig. 3c). In this case, the value of  $2\rho d$  is large and the second order of smallness must be taken into account.

To calculate the intensities of transmitted light taking into account the non-ideality of the PMT tube, it is necessary to first estimate the ratio  $f_1/f_2$  depending on the wavelength. From Fig. 3b it is evident that the value  $f_1/f_2$  should change abruptly at  $\lambda = 1050$  nm.

To estimate  $f_1/f_2 \approx 1 - h$  from experimental transmission spectra, we use the formula:

$$h \sin^2 \rho d = (I_p - I_s + \Delta I e^{-\xi}) / (I_p + I_s), \quad (12)$$

where  $\Delta I e^{-\xi}$  is taken to be equal to the difference between the experimental  $I_p$  and  $I_s$  at a wavelength of 2500 nm (for a thin sample  $\Delta I e^{-\xi} = 88.3 - 87.2 = 1.1$ ). In this case, since  $h$  is a small value, formula (12) gives correct results only for  $\sin^2 \rho d$  values close to unity. It is best to use points at which  $\sin^2 \rho d = 1$ . Therefore,  $f_1/f_2$  can only be estimated on a thick sample and at those wavelengths at which the  $\sin^2 \rho d$  value is sufficiently large.

For a thin sample, the  $f_1/f_2$  values were calculated in the range  $\lambda = 400$ –570 nm, in the rest of the range  $f_1/f_2$  was taken as a constant equal to 1.033 (the constant was chosen so that the resulting curve was smooth, Fig. 4a). The  $f_1/f_2$  values calculated at different wavelengths in the range  $\lambda = 400$ –570 nm were extrapolated by the dependence:

$$f_1/f_2 = -1.07 \times 10^4 - 1.63 \times 10^8/\lambda^2 + 2.05 \times 10^6/\lambda +$$

$$+ 29.71 \lambda - 0.046 \lambda^2 +$$

$$+ 3.82 \times 10^{-5} \lambda^3 - 1.31 \times 10^{-8} \lambda^4. \quad (13)$$

The results of calculating the transmitted light intensities using formulas (9), (10) with the obtained  $f_1/f_2$  (13) values (13) are shown in Fig. 4b, 4c for sample thicknesses of 1 and 10 mm. The values of  $I_{0p}$  and  $I_{0s}$  at  $\lambda = 2500$  nm for the  $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$  sample with a thickness of  $d = 1$  mm are taken as  $I_{0p}$  and  $I_{0s}$ :  $I_{0p} = 88.3$ ,  $I_{0s} = 87.2$ . It is evident that the obtained curves do not agree very well with the experimental ones, especially for a thickness of 10 mm. This is due to the fact that for a thin sample it is impossible to correctly calculate  $f_1/f_2$ , as well as to estimate the magnitude of the jump at  $\lambda = 1050$  nm (Fig. 3b).

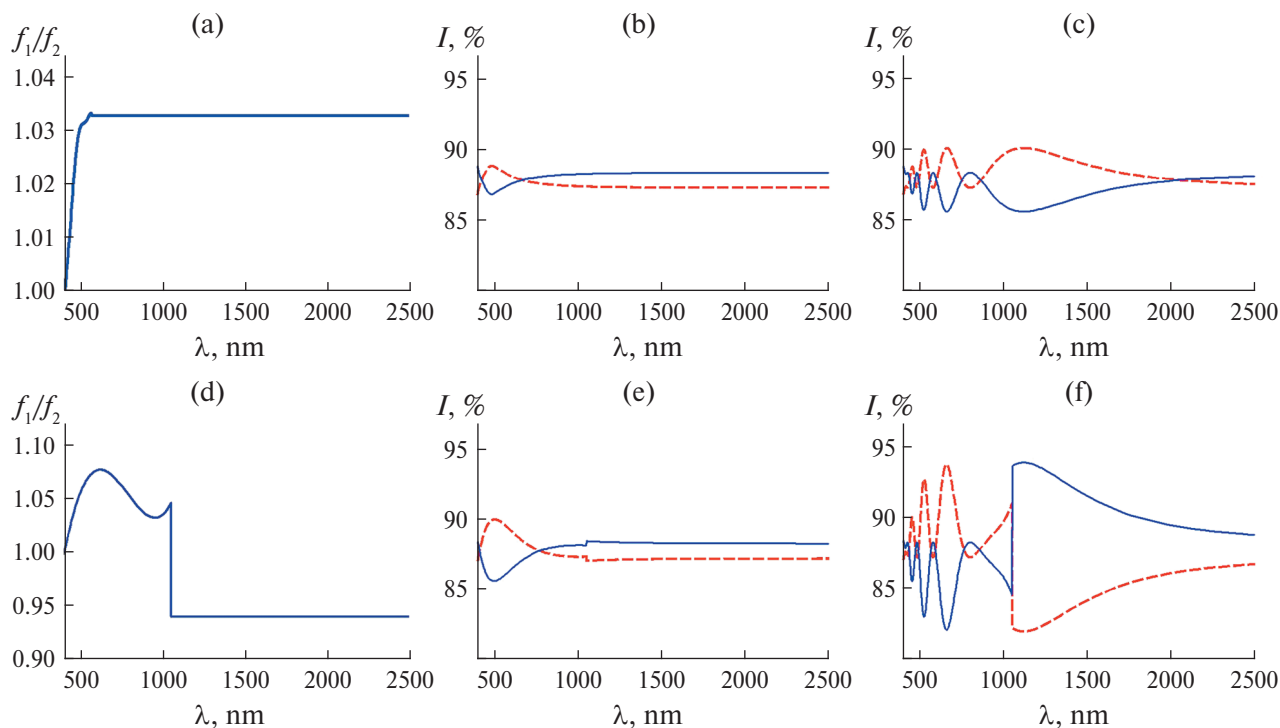
For a thick sample, we will calculate the values of  $f_1/f_2$  in the range  $\lambda = 400$ –1050 nm in accordance with formula (12), in the range  $\lambda \geq 1050$  nm we consider the ratio  $f_1/f_2$  to be a constant and take it equal to the average value obtained in the range  $\lambda = 1050$ –1200 nm,  $f_1/f_2 = 0.94$  (Fig. 4d). The results of the calculation of  $f_1/f_2$  in the range  $\lambda = 400$ –1050 nm are extrapolated by the dependence:

$$f_1/f_2 = -0.32 + 64.93/\lambda +$$

$$+ 5.02 \times 10^{-3} \lambda - 6.37 \times 10^{-6} \lambda^2 + 2.64 \times 10^{-9} \lambda^3. \quad (14)$$

The results of calculating the intensities of transmitted light with the given values of  $f_1/f_2$  are shown in Fig. 4e, 4f. The values of  $I_{0p}$  and  $I_{0s}$  are the same as in the previous case:  $I_{0p} = 88.3$ ,  $I_{0s} = 87.2$ . It is evident that the dependences obtained in Fig. 4e, 4f are in fairly good agreement with the experimental ones.

To obtain better agreement between the experimental and calculated transmission spectra, it is necessary to evaluate  $f_1/f_2$  over the entire range on thicker samples or on other sections, and also to take into account the absorption of the crystal.



**Fig. 4.** Calculation of  $f_1/f_2$  and transmitted light intensities for catangasite crystals at  $I_{op} = 88.3$  and  $I_0 = 87.2$ : a – calculation of  $f_1/f_2$  for a thin sample ( $d = 1$  mm), b, c – calculation of transmitted light intensities for thin (b) and thick (c) samples with the obtained  $f_1/f_2$  data; d – calculation of  $f_1/f_2$  for a thick sample ( $d = 10$  mm), d, e – calculation of transmitted light intensities for thin (d) and thick (f) samples with the obtained  $f_1/f_2$  data.

#### With polarizer and analyzer

The transmission spectra of thin samples of catangasite ( $d = 1$  mm), cut perpendicular to the optical axis, in polarized light at different positions of the polarizer and analyzer are considered in [17]. In this case, the non-ideality of the optical elements of the device was not taken into account. Let us consider how this non-ideality affects the transmission spectra and what error it introduces when calculating the values of optical activity.

The experimental transmission spectra for two samples of catangasite with different angles between the polarizer and the analyzer are shown in Fig. 5a, 5b. In this case, the polarizer is installed at a fixed angle  $\alpha$  ( $\alpha = 0$  is the  $p$ -polarization of the light incident on the crystal,  $\alpha = 90^\circ$  is the  $s$ -polarization), and the position of the analyzer  $\beta$  changes, the angle between the polarizer and the analyzer is designated  $\tau = \beta - \alpha$ . The measurements for the thick sample were carried out with an  $s$ -polarization wave incident on the crystal, and for the thin sample – with a  $p$ -polarization wave incident. All spectra, except for the case of parallel polarizers, have a “step” at  $\lambda = 1050$  nm.

For a  $z$ -cut with different angles  $\tau$  between the polarizer, analyzer and non-ideal PMT, we obtain:

$$I_{\pm\tau} = \frac{I_0}{2} e^{-\zeta} \frac{f_1 + f_2 + (f_1 - f_2) \cos 2\beta}{f_1 + f_2 + (f_1 - f_2) \cos 2\alpha} \times (\text{ch}\delta + \cos 2(p\delta \pm \tau)). \quad (15)$$

At  $\alpha = 0$  ( $p$ -polarization of incident light)

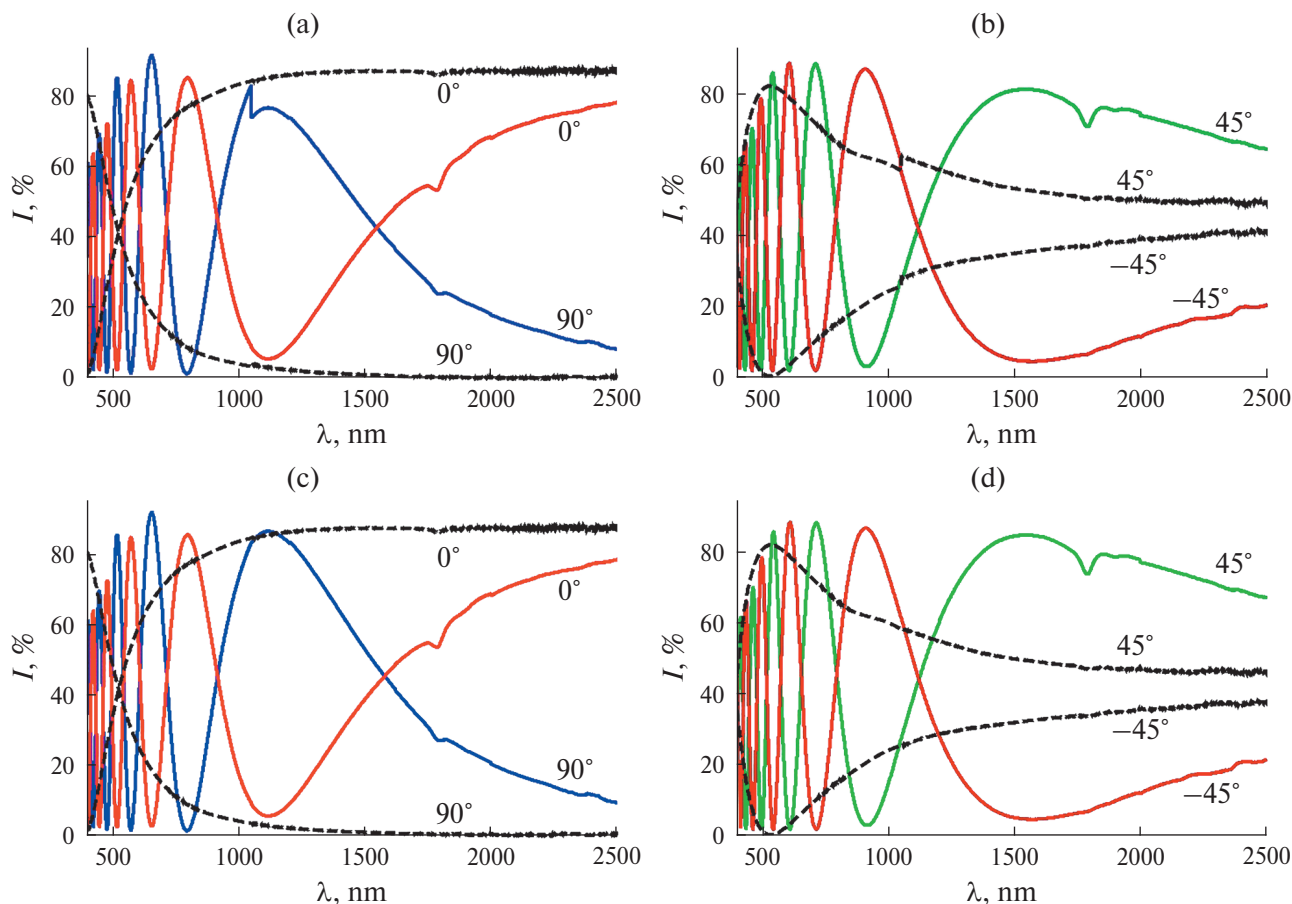
$$I_{\pm\tau} = I_0 e^{-\zeta} \frac{f_1 + f_2 + (f_1 - f_2) \cos 2\tau}{4f_1} \times (\text{ch}\delta + \cos 2(p\delta \pm \tau)), \quad (15a)$$

at  $\alpha = 90^\circ$  ( $s$ -polarization of incident light)

$$I_{\pm\tau} = I_0 e^{-\zeta} \frac{f_1 + f_2 - (f_1 - f_2) \cos 2\tau}{4f_2} \times (\text{ch}\delta + \cos 2(p\delta \pm \tau)). \quad (15b)$$

In this case, the parameters  $f_1, f_2$  are included only in a separate multiplier (formula (15) differs from the ideal one by multiplication by  $\frac{f_1 + f_2 + (f_1 - f_2) \cos 2\beta}{f_1 + f_2 + (f_1 - f_2) \cos 2\alpha}$ ).

The value of this multiplier depends on the initial position of the polarizer  $\alpha$ ; replacing  $\alpha = 0$  with  $\alpha = 90^\circ$  leads to a permutation of the coefficients  $f_1, f_2$ .



**Fig. 5.** Experimental spectra of  $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$  at different angles  $\tau$  between the polarizer and the analyzer: a, b – original, c, d – smoothed;  $\tau = 0^\circ$  and  $90^\circ$  (a, c),  $\tau = \pm 45^\circ$  (b, d). Solid lines – thick sample ( $d = 10$  mm), measurements with  $s$ -polarization; dotted line – thin sample ( $d = 1$  mm), measurements with  $p$ -polarization. For smoothed curves, the part of the spectrum at  $\lambda > 1050$  nm is multiplied by the value  $I(1049 \text{ nm})/I(1050 \text{ nm}) = 1.125$  for  $\tau = 90^\circ$ , 1.057 for  $\tau = -45^\circ$ , 1.046 for  $\tau = 45^\circ$  (thick sample), 0.873 for  $\tau = 90^\circ$ , 0.917 for  $\tau = -45^\circ$ , 0.939 for  $\tau = 45^\circ$  (thin sample).

At  $\lambda = 1050$  nm, the values  $f_1$  and  $f_2$  probably change abruptly, so the intensity also changes abruptly. In this case, with parallel polarizers ( $\beta = \alpha$ ,  $\tau = 0$ ), according to (15), there will be no abrupt change.

To obtain smooth curves, the right-hand side of the spectra in Fig. 5a and 5b can be renormalized by multiplying the transmission values  $I$  at wavelengths  $\lambda \geq 1050$  nm by the ratio  $I(1049 \text{ nm})/I(1050 \text{ nm})$ , which characterizes the relative shift of the curves (Table 1). Note that such smoothing of the curves does not take into account the difference in the  $\rho d$  at  $\lambda = 1049$  and  $1050$  nm. It is evident that when  $p$ -polarized light falls on the crystal, the value of  $I(1049)/I(1050)$  is less than unity, and for  $s$ -polarized light, it is greater than unity. In this case, the relative shift of the curves is maximum for the case of crossed polarizers. The smoothed transmission spectra are shown in Fig. 5c and 5d.

Let us calculate  $I(1049 \text{ nm})/I(1050 \text{ nm})$  from formulas (15a) and (15b) for both cases, using expression (14) for  $f_1/f_2$  at  $\lambda = 1049$  nm and  $f_1/f_2 = 0.94$  at  $\lambda = 1050$  nm. From Table 1 it is evident that the calculated

**Table 1.** Experimental and calculated values of  $I(1049 \text{ nm})/I(1050 \text{ nm})$

Ca <sub>3</sub> TaGa <sub>3</sub> Si <sub>2</sub> O <sub>14</sub> Sample	$\tau$ , deg	$I(1049 \text{ nm})/I(1050 \text{ nm})$	
		experiment	calculation
$d = 1$ mm	–45	0.917	0.947
	45	0.939	0.948
	90	0.873	0.902
$d = 10$ mm	–45	1.057	1.059
	45	1.046	1.043
	90	1.125	1.111



values of  $I(1049 \text{ nm})/I(1050 \text{ nm})$  agree quite well with the experimental ones, especially for the thick sample.

*Accounting for PMT non-ideality in the calculation of light polarization plane rotation angle  $\rho$ .* We will assume that  $\alpha = 0^\circ$ . Since circular dichroism is very small, we will take  $\delta = 0$ . For parallel and crossed polarizers:

$$I_{\perp} = I_0 \frac{f_2}{f_1} e^{-\zeta} \sin^2 \rho d, \quad I_{\parallel} = I_0 e^{-\zeta} \cos^2 \rho d,$$

$$\rho d = \arctg \sqrt{\frac{f_1}{f_2} \frac{I_{\perp}}{I_{\parallel}}}. \quad (16)$$

at  $\tau = \pm 45^\circ$ :

$$I_{\pm 45} = \frac{I_0}{4} \frac{f_1 + f_2}{f_1} e^{-\zeta} (1 \pm \sin 2\rho d),$$

$$\rho d = \frac{1}{2} \arcsin \left[ \frac{I_{45} - I_{-45}}{I_{45} + I_{-45}} \right]. \quad (17)$$

To obtain formulas with  $\alpha = 90^\circ$ , you need to swap  $f_1$  and  $f_2$ .

The value does not change with a non-ideal photomultiplier, and this agrees with the fact that the curve with parallel polarizers does not have a jump at  $\lambda = 1050 \text{ nm}$ . According to (15)–(17), the maximum relative shift of the curves at  $\lambda = 1050 \text{ nm}$  should be

$\tau = 90^\circ$  with crossed polarizers, which agrees with the experimental results obtained (Fig. 5a, Table 1). The position of the maxima and minima does not depend on  $f_1, f_2$ , but the intersection points of the curves depend on these values. For example, in the case where instead of  $\text{tg}^2 \rho d = 1$  and  $\rho d = \pi/4$  we obtain  $\text{tg}^2 \rho d = f_2/f_1$  and the intersection of the curves will deviate from the point  $\rho d = \pi/4$ .

In the case of  $\tau = \pm 45^\circ$ , the quantities  $f_1, f_2$  are included in the formulas equally for both  $\tau = +45^\circ$  and  $\tau = -45^\circ$ , and do not affect the position of the intersection points of the curves and . In addition, from (17) it is clear that for  $\tau = \pm 45^\circ$ , the non-ideality of the photomultiplier does not affect the result of calculating  $\rho$  (the parameters  $f_1, f_2$  are not included in the expression for  $\rho d$ ).

*Accounting for polarizer and analyzer imperfections in optical activity calculations.* Let us consider the effect of non-ideality of the polarizer and analyzer on the transmission spectra. For simplicity, we assume that the values of the greatest and least transmission  $p_1$  and  $p_2$  of the polarizer and analyzer are the same. When normalizing, we assume that without a sample, with parallel polarizers, the transmission is 100%, and with crossed polarizers, it is 0%. Therefore, we subtract the transmission value of crossed polarizers without a sample from the obtained intensity. Then, with an ideal PMT, we obtain:

$$I_{\pm\tau} = \frac{I_0}{2} e^{-\zeta} \frac{(p_1 + p_2)^2 \text{ch}\delta - 4p_1 p_2 + (p_1 - p_2)^2 \cos 2(\rho d \pm \tau)}{2(p_1^2 + p_2^2)}. \quad (18)$$

Since circular dichroism in transparent crystals is very small, we assume that  $\delta = 0$ . Then:

$$I_{\pm\tau} = \frac{I_0}{2} e^{-\zeta} \frac{(p_1 - p_2)^2}{2(p_1^2 + p_2^2)} (1 + \cos 2(\rho d \pm \tau)). \quad (19)$$

Thus, the non-ideality of the polarizer without taking into account the non-ideality of the PMT leads only to the appearance of a constant multiplier, which does not in any way affect the calculation of optical activity.

*Correction for non-ideal polarizer, analyzer and PMT in optical activity measurements.* When taking into account the above imperfections, the general expression for the intensity of the transmitted light is very cumbersome. Therefore, we will give expressions only for the values  $\tau = 0^\circ, \pm 45^\circ$  and  $90^\circ$  in the approximation  $\delta = 0$ .

At  $\tau = 0^\circ, 90^\circ$ :

$$I_{\parallel} = I_0 e^{-\zeta} \frac{(p_1 - p_2)(f_1 p_1 - f_2 p_2)}{(f_1 p_1^2 + f_2 p_2^2)} \cos^2 \rho d, \quad (20)$$

$$I_{\perp} = I_0 e^{-\zeta} \frac{(p_1 - p_2)(f_2 p_1 - f_1 p_2)}{(f_1 p_1^2 + f_2 p_2^2)} \sin^2 \rho d. \quad (21)$$

Leaving only the terms of the first order of smallness, we obtain:

$$\frac{I_{\perp}}{I_{\parallel}} = \frac{(f_2 p_1 - f_1 p_2)}{(f_1 p_1 - f_2 p_2)} \text{tg}^2 \rho d \approx \frac{f_2}{f_1} \text{tg}^2 \rho d. \quad (22)$$

Thus, the non-ideality of polarizers at  $\tau = 0^\circ, 90^\circ$  introduces an error in the calculation of  $\rho$  only in the second order of smallness.

At  $\tau = \pm 45^\circ$

$$I_{\pm 45} = I_0 e^{-\zeta} \frac{(f_1 + f_2)(p_1 - p_2)^2 (1 \pm \sin 2\rho d) + 2(p_1 - p_2)(f_1 - f_2) \sqrt{p_1 p_2} \cos 2\rho d}{4(f_1 p_1^2 + f_2 p_2^2)}. \quad (23)$$

From this expression it can be deduced that in this case, too, the non-ideal polarizer and analyzer introduce an error in the calculation of  $\rho$  in the second order of smallness, since the resulting addition to the intensity is proportional to the product of small values  $h$ .

Thus, the error in calculating  $\rho$  associated with the non-ideality of the photomultiplier is generally much greater than the error associated with the non-ideality of the polarizer and analyzer. At the same time, the considered measurement imperfections do not affect the calculation of optical activity based on the maxima and minima of intensities (15)–(17), so such a calculation is the most accurate, but it is possible only for large values of  $\rho d$ .

It should be noted that the greatest error in calculating  $\rho$  is obtained with its small values and the use of formulas (16) for parallel and crossed polarizers. In this regard, expression (16) is not suitable for calculating  $\rho$  in the IR region, where the optical activity is low. In addition, there is an error in calculating the optical activity associated with the non-ideality of the PMT. In accordance with formulas (15), (17), the most accurate results of calculating  $\rho$  should be at an angle of  $\tau = \pm 45^\circ$ . In the approximation of an ideal PMT, the calculation at  $\tau = \pm 45^\circ$  also gives the most accurate results [17].

## CONCLUSION

Theoretical and experimental studies of the spectra of transmission coefficients of catangasite crystals  $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$  of different thickness (1 and 10 mm), cut perpendicular to the optical axis, were carried out, taking into account the imperfection of the optical elements of the spectrophotometric complex (polarizers and PMT).

When measuring in unpolarized light, the transmission coefficient spectra show jumps at wavelengths  $\lambda = 720$  and  $1050$  nm, most noticeable on a 10 mm thick sample. However, no such jumps are observed for optically inactive  $\text{LiNbO}_3$  and  $\text{Gd}_3\text{Al}_2\text{Ga}_3\text{O}_{12}:\text{Ce}$  crystals.

The transmitted light intensities measured with one polarizer for  $p$ - and  $s$ -polarizations of incident light are different. For a thick sample, pronounced jumps are observed on the curves at  $\lambda = 1050$  nm. The difference between the obtained spectra is due to the non-ideality of the PMT and the magnitude of the rotation of the plane of polarization of light  $\rho d$ , which is much greater for a thick crystal. An estimate of the PMT parameters and their dependence on the wavelength is made from experimental data.

In measurements with a polarizer and analyzer, the non-ideality of the PMT leads to a jump in the transmission spectra at  $\lambda = 1050$  nm, which can be eliminated by multiplying by a constant. The non-ideality of the polarizers and PMT does not affect the position of the maxima and minima of the transmitted light intensities and, accordingly, the result of calculating

$\rho$  from the maxima and minima on a thick sample (10 mm). If the sample thickness is small (1 mm), the rotation of the plane of light polarization  $\rho$  is calculated from the ratios of the intensities of the transmitted light at different angles between the polarizer and the analyzer. In this case, the main contribution is made by errors associated with the non-ideality of the PMT and with the small value of optical activity. Both of these errors are maximum for the case of crossed polarizers, so the calculation based on the intensity ratio for crossed and parallel polarizers can give a large error, especially in the IR region. In this case, for a more accurate result, transmission spectra measured at angles between the polarizer and the analyzer of  $\pm 45^\circ$  are required.

The obtained measurement errors depend on the change of optical elements in a specific device.

## ACKNOWLEDGMENTS

The authors express their gratitude to JSC Fomos-Materials and personally to O.A. Buzanov for providing crystal samples.

## FUNDING

The work was carried out within the framework of the state assignment of the National Research Center “Kurchatov Institute” in terms of calculating the optical parameters of crystals and taking into account the imperfection of the optical elements of the spectrophotometer. Measurements of the transmission spectra of crystals were carried out at the MUIL PPMiD “Single crystals and blanks based on them” with the financial support of the Ministry of Education and Science of Russia within the framework of the state assignment to universities FSME-2023-0003.

## CONFLICT OF INTERESTS

The authors of this work declare that they have no conflicts of interest.

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