Birefringence in $CdGa_2S_4$ Crystals

Tiron A.V., Parvan V.I., Syrbu N.N.
Technical University of Moldova,
Chisinau, Republic of Moldova

V.V. Zalamai
Institute of Applied Physics,
Academy of Sciences of Moldova,
Chisinau, Republic of Moldova

***Abstract* – In $CdGa_2S_4$ crystals Fabry-Perot and birefringence interference spectra were investigated. Spectral dependences of refraction indexes for ordinary and extraordinary light waves are defined. The spectral dependence $\Delta n = n_e - n_o$ from the short and long-wavelength parts of isotropic wavelength is determined. It is established that at $\lambda > \lambda_0$ Δn is positive and at $\lambda < \lambda_0$ Δn is negative. Wavelength λ_0 = 485.7 nm shifts with decreasing temperature to short-wavelengths. The band in reflection spectra observed at the isotropic wavelength has a small halfwidth (∽3 - 5 Å). Another isotropic wavelength was found in the short-wavelength region (433 nm) for crystals obtained by iodine transport method.**

***Keywords* – cadmium thiogallate; birefringence; interference spectra; ordinary and extraordinary waves; isotropic wavelength;**

I. Introduction

Crystals of cadmium thiogallate ($CdGa_2S_4$) belong to the wide class of triple chalcogenide compounds $A^{II}B_2^{III}C_4^{VI}$, and crystallize in a lattice with space group S_4^2. The crystals have a birefringence, optical activity and a significant value of nonlinear susceptibility coefficient. Birefringent properties of thiogallate cadmium were studied in Ref. [1 - 5]. Optical properties and energy band structure of crystals $CdGa_2S_4$ were investigated [6 - 10]. The Raman scattering, infrared vibrational modes and the effect of pressure on vibrational modes are considered in Ref. [11 - 15]. Photovoltaic and emission characteristics and the spectrum of local states $CdGa_2S_4$ investigated in several studies [16 - 19]. High photosensitivity, bright photoluminescence in conjunction with a wide band-gap promote the use of these compounds in semiconductor devices. Crystals of this group are already used in various devices of nonlinear optics and optical filters [20 - 23]. Therefore comprehensive investigation of physical properties of $CdGa_2S_4$ crystals is important today.

New data of the optical properties anisotropy studies of $CdGa_2S_4$ crystals are presented and Fabry-Perot and birefringence interference spectra are considered in this paper. From the experimental data, the spectral dependences of the refractive indices for the ordinary and extraordinary light waves, their difference and its phases difference were determined.

II. Experimental Methods

Bulk crystals of $CdGa_2S_4$ which grown up by Bridgman method had the size 1x3cm. Crystals grown without iodine and iodine transport method in ampoules are plates with mirrored surfaces - 3x4x10 mm. The surfaces of most plates are parallel to the axis c. Low-temperature spectra of the crystals placed in the closed helium cryostat LTS-22 C 330 optical cryogenic system were measured on MDR-2 with resolution 0.5 meV. Optical systems are completely automated and provide data in look of data files. Optical reflection spectra were measured also on SPECORD-M40 spectrometer with data recording on the PC.

III. Experimental Results and Discussions

A characteristic feature of thiogallate cadmium ($CdGa_2S4$) is the dispersion of the refractive indices no and ne near the absorption edge. In thiogallate cadmium crystals the crossing of spectral dependences no and ne at long-wavelength side of the absorption edge was observed. Fig. 1 shows the interference of the transmission spectra of $CdGa_2S_4$ crystals of thickness 53 μm in polarizations E||c and E⊥c. Fig. 1, B shows the spectral dependence of n_o and n_e calculated from spectra of the Fabry-Perot interference using ratio $n = M/(2d*(1/\lambda_1-1/\lambda_2))$ [24], where M = 1 if λ_1 and λ_2 corresponds to wavelengths of adjacent minima or maxima in the interference spectrum. Fig.1, C shows the spectral dependence of the refractive index difference $\Delta n = n_e - n_o$ at 300 K.

Spectral dependences of no and ne intersect at wavelength λ_0 = 487 nm, which is isotropic wavelength. Investigating the dispersion of birefringence crystals $CdGa_2S_4$ by interference of polarized rays in [1 - 4], it was found that the isotropic wavelength λ_0 = 4909 Å. Previously in work [6] we reported that the isotropic wavelength at 300 K is 485.6 nm. Spectral dependences $\Delta n = n_e - n_o$ at 300 K cross the zero axis at wavelengths 485.6 - 487 nm (see Fig. 1, C). At passing via the wavelength λ_0 = 487 nm birefringence changes the sign, that is, from optically positive in the spectral region $\lambda < \lambda_0$ crystal becomes optically negative in the region $\lambda > \lambda_0$.

Transmission spectra T of crystals $CdGa_2S_4$ in parallel rays of crossed polarizers when c axis of the crystal is parallel to the polarization direction of one of the polarizers, is characterized by narrow transmission band, localized at wavelengths of λ = 485 - 487 nm (Fig. 2, A). In the case of unidirectional polarizers narrow absorption line in the same spectral region was observed. The transmission spectra of crystals $CdGa_2S_4$ placed between crossed polarizers in the converging rays at 300 K show a more pronounced interference with intense peaks at around λ_0 (Fig. 2, A). By choosing the thickness of the crystals it is possible to reduce the number of side maxima and receive isolate maximum at wavelength λ_0. The transmission of the crystal in crossed polarizers at isotropic wavelength depends on the thickness of the crystal $CdGa_2S_4$ Fig. 2, B.

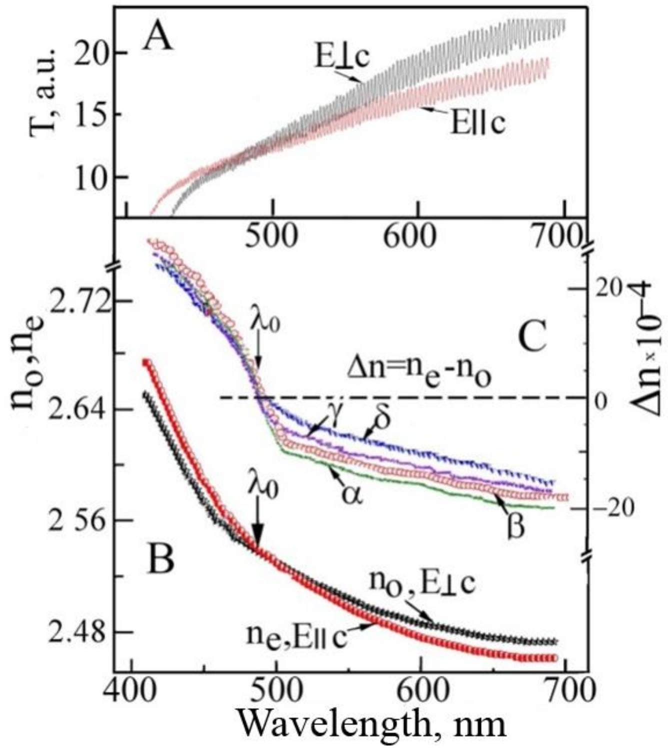

Fig.1 A Fabry-Perot interference of the transmission spectra of $CdGa_2S_4$ crystal with thickness 53 μm in polarizations E||c and E⊥c, B - spectral dependence of n_o and n_e and C - spectral dependence of $\Delta n = n_e - n_o$ at 300 K for samples with thicknesses d - 30 μm (α), 110 μm (β), 75 μm (γ) and 45 μm (δ).

Fig. 3, A shows transmission spectra interference of crystals $CdGa_2S_4$ of thickness 5.9 mm deposed between crossed polarizers at 300 K. The absorption calculated from these spectra is shown on Fig. 3, B. In such crystals Fabri-Perot's interference does not occur and the observed spectra are caused by birefringence interference. This is due to the fact that at a wavelength λ_0, where $\Delta n(\lambda_0) = 0$, the phase difference $\Delta\Phi(\lambda_0)$ between the two mutually perpendicular polarized modes propagating in the crystal is always equal to zero. Thus in the birefringence interference spectra at the wavelength λ_0 is always observed either the full maximum (parallel polarizers) or zero minimum (crossed polarizers), independently of the crystal thickness. The wavelength of maximum (minimum) corresponds to the order of interference k = 0.

At the calculations of the refractive index spectral dependence from the interference of polarized beams, it is necessary to determine the sequence number k of the interference spectra, which are described by the expression:

$$\Delta n(\lambda)d=k\lambda, \quad (1)$$

where d - crystal thickness. Determination of the line for which k = 0 in the interference spectra is possible at the dispersion $\Delta n(\lambda)$ investigation of crystals with isotropic point (IP). Considering this, one can assign the order of any interference line. The study of birefringence crystals $CdGa_2S_4$ in crossed polarizers [4 - 6] shown that the amplitude of the band corresponding to k = 0, is not a constant, and depends on the crystal thickness. The transparency value of $CdGa_2S_4$ crystals in crossed polarizers is depended on a thickness as shown on Fig. 2, B.

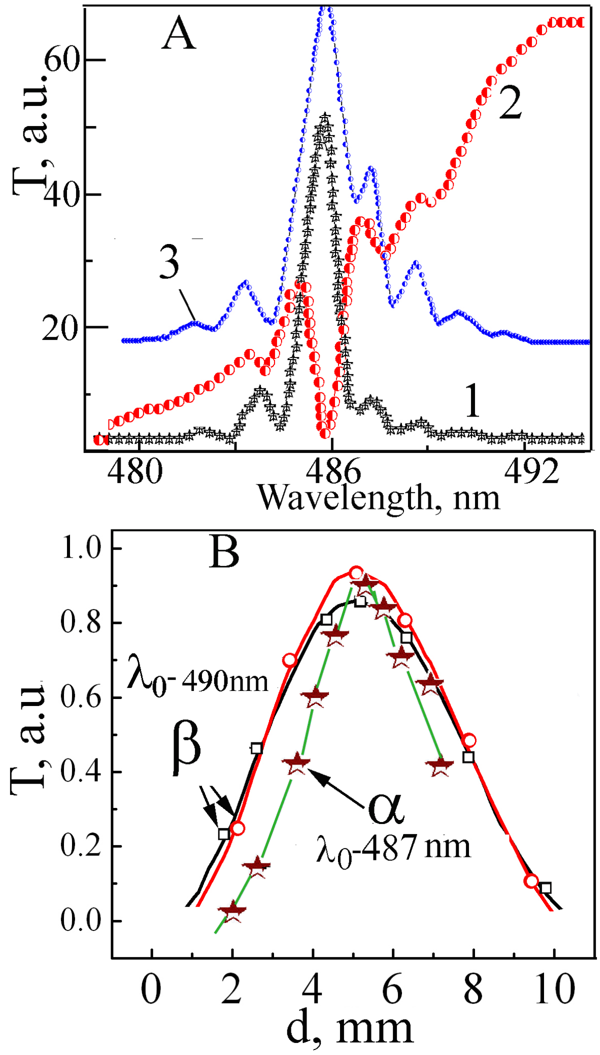

Fig.2. A - Transmission spectra of $CdGa_2S_4$ crystals at 300 K placed between crossed (1 and 3 - Ref. [4, 5]) and parallel polarizers (2), B - dependence λ_0 on the crystal thickness (the results of present work - α and the results of Ref. [4, 5] - β).

Transmission spectrum of a system consisting of two parallel exposed polarizers and located between the plane-parallel crystal $CdGa_2S_4$ thickness d = 5.9 mm with the optical axis at an angle of 40 - 50° to the principal directions of the polarizers, has the form shown in Figure 3. At a wavelength of λ_0 = 487 nm maximum is observed, with almost zero intensity. Relatively a given wavelength interference maxima in $\lambda > \lambda_0$ marked numbers from -1 to -12. In the wavelength region $\lambda < \lambda_0$ detected peaks 1 - 17, fig. 3, A and B. From the interference of the transmission spectra calculated the absorption coefficient in the entire measured range, Fig. 1, B. Absorption coefficient in the bands numbered from -7 to -11 is changed 103 times. In [5] theoretically examined the mechanism of the appearance of the band k = 0 in the transmission spectra of a system consisting of two crossed polarizers and is located between the crystal $CdGa_2S_4$. We consider the change in intensity of the band as k = 0, the transmission spectra of crystals, when the thickness of the crystals placed between the polarizers. Transmission at λ_0 depending on d varies sinusoidally from minimum to maximum.

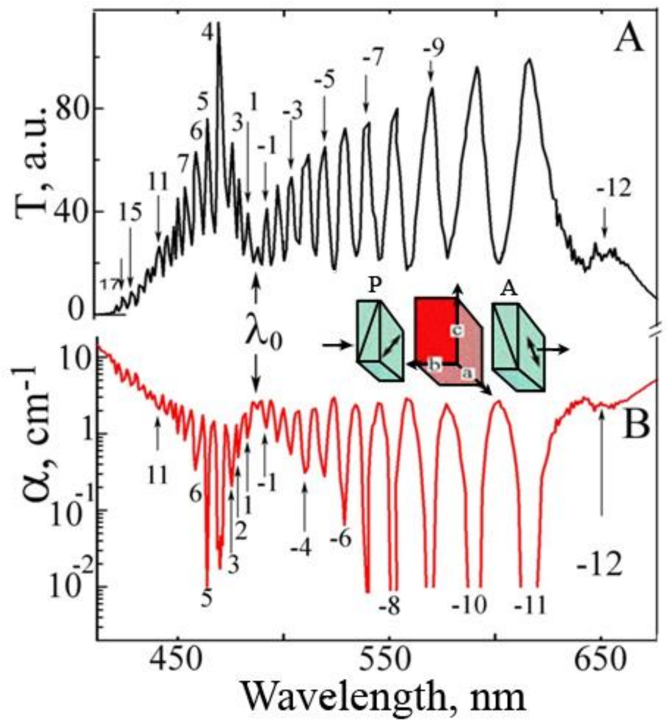

Fig. 3 Spectral dependence of transparency T (A) and absorption α, cm^{-1} (B) of the crystals $CdGa_2S_4$ of thickness 5.9 mm in crossed polarizers at 300 K with the orientation c axis at an angle 45° to the orientation of polarizers.

In uniaxial crystals $CdGa_2S_4$ having birefringence ($\Delta n(\lambda)$) and optical activity phenomenon the interference of polarized beams is due to the fact that in the crystal are distributed two elliptically polarized modes, the phase shift $\Delta\Phi$ between them is given by equation [5]:

$$\Delta\Phi = \frac{2\pi}{\lambda} d \left[\Delta n^2 + \left(\frac{G}{n^*} \right)^2 \right]^{1/2}, \qquad (2)$$

where G - the gyration parameter, $n^* = (n_e + 2n_o)/3$ the average refractive index. For the crystal $CdGa_2S_4$ (Symmetry S_4^2) the parameter of gyration is described by relation:

$$G = \pm\left[g_{11}\left(l_1^2 - l_2^2 \right) + 2 g_{12} l_1 l_2 \right], \qquad (3)$$

where g_{11} and g_{12} are independent, non-zero components of the gyration tensor; l_1 and l_2 are direction cosines defining the direction of light propagation with respect to the axes [100] and [010] crystal. The sign "±" indicates that depending on the choice of the axes [100] and [010] as a basic change the direction of rotation of the polarization plane. If the radiation propagates along [100] axis, then $G = \pm g_{11}$. Phase shift at a wavelength λ_0 is:

$$\Delta\Phi = \frac{2\pi d g_{11}}{n^* \lambda_0}. \qquad (4)$$

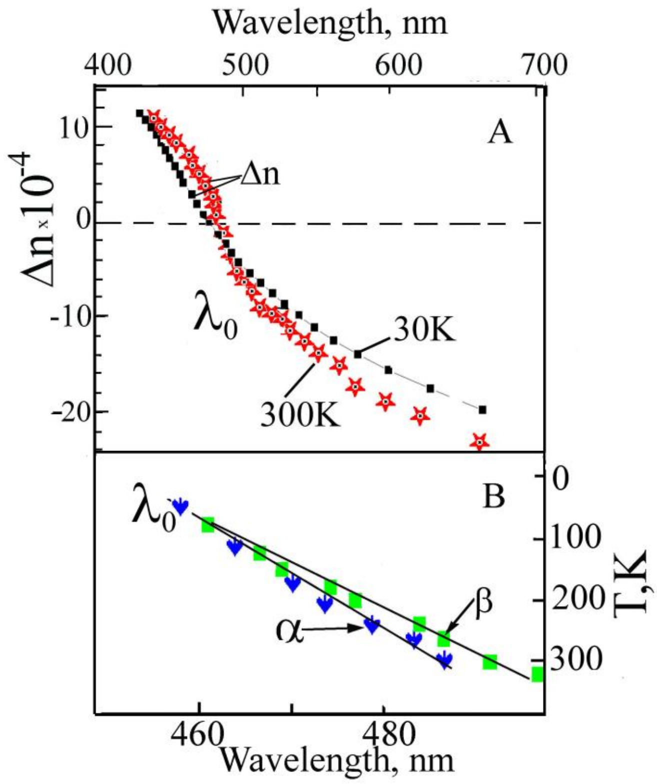

Fig. 4 A - spectral dependence of $\Delta n = n_e - n_o$ calculated from the interference fringes (1 - 13 and from -1 to -17), the crystal thickness d = 5.9 mm. B - the temperature dependence of λ_0 (the results of this work (α) and the results of Ref. [1 - 5] (β)).

Ellipses degenerate into a circle and in the crystal two circularly polarized waves in opposite directions distribute. At a wavelength of IP own rotation of the polarization plane of incident light on the crystal takes place. The polarization plane rotation angle measurements at wavelength λ_0 = 532 nm for crystal $CdGa_2S_4$ give value of the specific rotation $\rho(\lambda_0) = 11 \pm 3$ grad/mm. Almost the same value was reported in Ref. [1 - 5]. Using the relation $\rho = \pm \pi g_{11}/n^*\lambda_0$ and value $n(\lambda_0) = 2.53$, it is obtained $g_{11}(\lambda_0) = 0.9 - 4$.

From equation (4) it is clear that all parameters are parameters of the crystal. By manipulating the crystal thickness, it is possible to achieve conditions then between two interference fringes with k = ±1 a band with k = 0 is detected.

The spectral dependence of $\Delta n = n_e - n_o$ calculated from the interference fringes 1 - 17 and from -1 to -12 for a crystal thickness d = 5.9 mm is shown on Fig. 4. In the wavelength region $\lambda < \lambda_0$ value of $\Delta n = n_e - n_o$ is positive and in the $\lambda > \lambda_0$ it is negative. The order of change Δn determined from the Fabry-Perot interference in the plane-parallel plates $CdGa_2S_4$ (Fig. 1) and form the interference of birefringence (Fig. 4) are almost identical. Fig. 4, B shows the temperature dependence of λ_0 of crystals studied in this work (curve α) and data according to the results of Ref. [1 - 5] (curve β). In these references the isotropic wavelength of $CdGa_2S_4$ crystals was observed at wavelength of 490.9 nm.

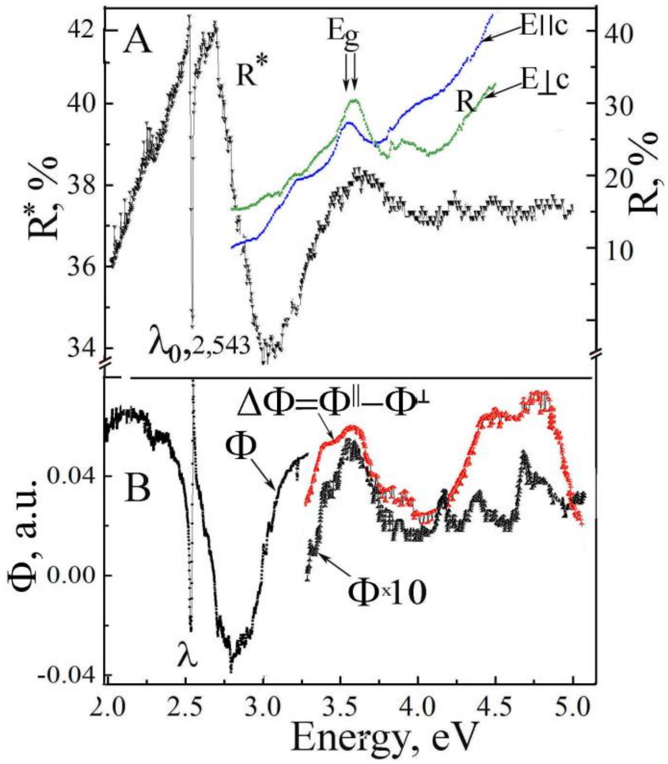

Fig. 5 A - Reflectance spectra R in polarizations E||c and E⊥c and reflection spectra R* in crossed polarizers of $CdGa_2S_4$ crystals at 300 K, B - spectral dependence of reflected rays phase φ in crossed polarizers and phase difference ($\Delta\Phi = \Phi^{\|} - \Phi^{\perp}$) obtained from reflection spectra in polarizations E||c and E⊥c.

Figure 5, A shows the reflection spectra R in polarizations E||c and E⊥c and reflection spectra R* in crossed polarizers of $CdGa_2S_4$ crystals measured at 300 K. A narrow band for which the reflection coefficient decreases sharply at isotropic wavelength λ_0 (2.543 eV) was observed in reflection spectra crystal deposed in crossed polarizers. For some crystals, the half-width of this band does not exceed 3 - 5Å. Weak features in energy minimum of band gap Eg were revealed in reflection spectra R* at short-wavelengths. Features in reflection spectra of these crystals at the same energies were observed in E||c and E⊥c polarizations as reported by our group in Ref. [6]. These features are due to direct transitions from the valence band to the conduction band with possible participation of excitons in the center of the Brillouin zone. The binding energy of excitons is equal to 51 -53 meV [6]. Using Kramers-Kronig relations from reflectance spectra R and R* phase (Φ) and phase difference ($\Delta\Phi = \Phi^{\|} - \Phi^{\perp}$) of reflected rays were calculated, Fig. 5, B. The spectra clearly show that sharp phase change occurs in vicinity of λ_0 and near the singularities of the electronic transitions.

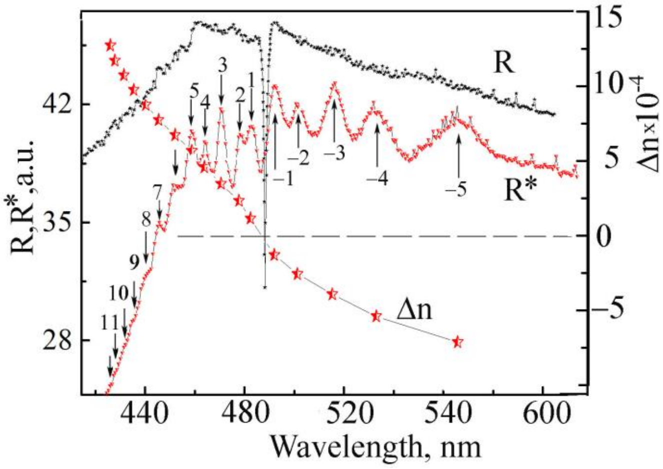

Fig. 6 Reflectance spectra R (**c** axis of the crystal is parallel to the orientation of polarizer), and R* (c axis has an angle of 30 - 40˚ with polarizer orientation) in crossed polarizers of $CdGa_2S_4$ crystals of thickness 1.9 mm at 300 K and Δn calculated from spectrum R*.

The characteristic interference lines 1 - 11 and (-1) - (-5) were observed in reflection spectra R* for crystals deposed between crossed polarizers at an angle 30 - 40° with polarizers orientation. This interference is the interference of the birefringence and not the interference of a Fabry-Perot (back side of the crystal was lusterless). Bands 1 - 11 and (-1) - (-5) gather to shorter wavelengths. Refractive indices difference Δn was defined taking into account bands numbers and crystal thickness (1.9 mm). The spectral dependence of Δn (Fig. 6) coincides with one defined from interference transmission spectra (Fig. 1) of crystals deposed between crossed polarizers.

In $CdGa_2S_4$ crystals when passing through the wavelength 487 nm wavelength region of the spectrum to longer sign changes from positive to negative, Fig. 1, Fig. 4. Δn change from positive to negative in CdGa2S4 crystals at passing via wavelength λ_0 = 487 nm from short- to long-wavelength spectral region (see Fig. 1 and Fig. 4). Therefore for $\lambda < \lambda_0$ $\Delta\Phi > 0$ and $\gamma < 0$ because $|d\Delta n/d\lambda| < 0$, i.e., with wavelength (λ) increasing the phase difference between ordinary and extraordinary modes per unit crystal thickness (ΔΦ/δ) decreases. In the $\lambda < \lambda_0$ the phase velocity of extraordinary wave is greater than the phase velocity of ordinary and $\Delta\Phi > 0$, (Fig. 7, A). The amplitude value of ΔΦ recorded experimentally is shown on Fig. 7, B. When $\lambda = \lambda_0$ the phase velocities of the two modes are equal and $\Delta\Phi = 0$. This wavelength is isotropic. At $\lambda > \lambda_0$ the phase velocity of ordinary wave exceeds the phase velocity of extraordinary and $\Delta\Phi < 0$ The sign of dΔΦ/d does not change, that is $\gamma < 0$. This means, that the phase difference (ΔΦ) in absolute values increases (Fig. 7, B). However, the value of $|d\Delta n/d\lambda|$ decreases then λ increasing. At the same time, the contribution due to Δν/λ increases. The sign of Δn accounting in this spectral region leads to decreasing of augmentation rate ΔΦ/δ with λ rise.

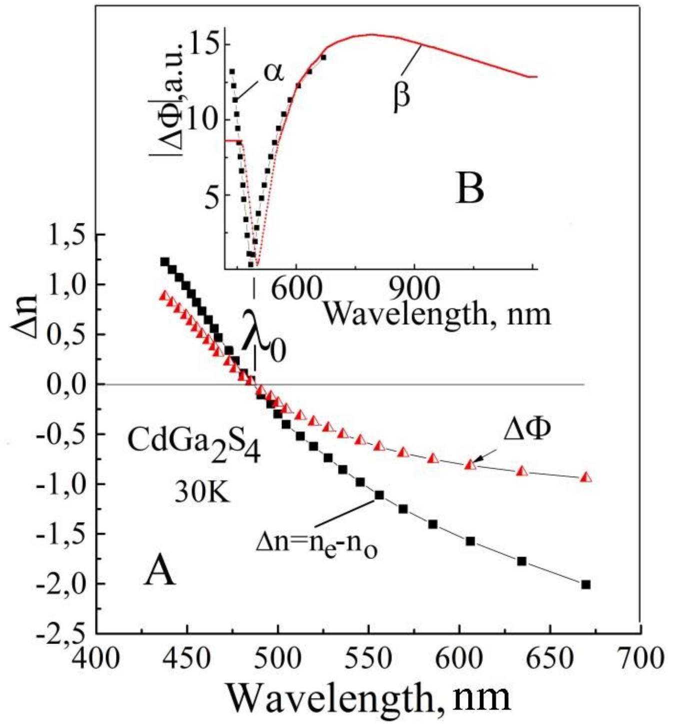

Fig. 7 A spectral dependence of $\Delta n = n_e - n_o$ and phase $\Delta\Phi$ of $CdGa_2S_4$ crystals at 30 K, B - the amplitude value of phase experimentally recorded at 30 K (α - results of this study, β - results at 300 K [4, 5].

An interaction between ordinary and extraordinary waves takes place in the vicinity of isotropic wavelength, and leads to energy transfer from one wave to another. The optical activity of crystals plays certain role in this phenomenon. Passed crystal light remains linearly polarized in IP [6]. Hence there is an interaction of two circularly polarized in opposite directions waves. After passing through the crystal waves acquired phase difference, defined by the specific rotation ρ of crystal. $CdGa_2S_4$ crystals have natural optical activity. For reasons of symmetry, the optical activity along c axis of $CdGa_2S_4$ crystal absent and reveals only in directions perpendicular to the optical axis, where it is weak compared with the linear birefringence. The specific rotation value of polarization plane for light propagating in direction [100] according to Ref. [4, 5] is 16.87 deg/mm. A lot of papers noted that the spectral position of IP and rotational ability of $CdGa_2S_4$ depend on the technology of crystal obtaining (temperature, pressure and other external factors) [4, 5]. Fig. 8 shows the transmission spectra T and dT/dλ in crossed polarizers of crystals CdGa2S4 with different thicknesses (1.9 mm (a), 1.65 mm (b) and 0.73 mm (c)) grown by iodine transport method. The crystals weren't doped specifically. Initial components (Cd, Ga and S) correspond to the purity level B4 as for crystals grown by Bridgman method thick spectra are discussed above (the concentration of impurity elements in the initial components does not exceed 0.0003%).

The transmission spectra of crystals obtained by iodine transport method and deposed between crossed polarizers have a transmission band λ_0 at a different wavelength (433 nm -2.86 eV). The crystals were prisms with dimensions 2x2x10 mm and had almost mirror-like surfaces. Reflection spectra in the intrinsic region were almost identical with one presented in our previous work [6]. Spectral dependences of refractive indices in polarizations E||c and E⊥c were determined from reflection spectra by using of Kramers-Kronig analysis (Fig. 8, B). Spectral dependences of refractive indices have features at energies of direct electronic transitions in the region from E_g to 6 eV. In the region $E < E_g$ the refractive index change in both polarizations, but the polarization E||c it change strongly. The last one leads to the curves no and ne intersection at smaller wavelengths (Fig. 8 B). In the short-wavelength region in both types of crystals were observed features (A, B and C) at energies coincide with exciton transition energies.

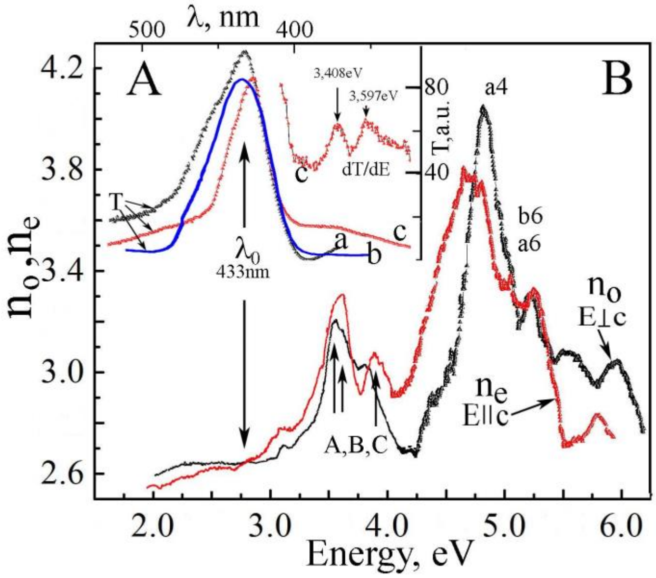

Fig. 8 A - transmission T and dT/dλ spectra in crossed polarizers of crystals $CdGa_2S_4$ with thicknesses 1.9 mm (a), 1.65 mm (b) and 0.73 mm (c) grown by iodine transport method, B - spectral dependences of the refractive indices n_o and n_e for these crystals.

CONCLUSIONS

Spectral dependences of refractive indices for ordinary no and extraordinary ne light waves were determined for $CdGa_2S_4$ crystals by investigations of interference Fabry-Perot spectra. Curves of abovementioned refractive indices intersect at wavelength λ_0 = 485.7 nm (isotropic wavelength). The spectral dependence $\Delta n = n_e - n_o$ were defined from birefringent interference spectra. It was found that Δn is positive and negative in the case of $\lambda > \lambda_0$ and $\lambda < \lambda_0$, respectively. The isotropic wavelength λ_0 shifts to short-wavelengths at temperature decreasing. The difference between phases of ordinary and extraordinary waves were calculated for $\lambda > \lambda_0$ and $\lambda < \lambda_0$. The value of absorption coefficient changes in 103 times into the points of these features. Such structure can be used as comb filter for corresponding wavelength.

The sharp line with low refractivity at isotropic wavelength (λ_0 = 485.7 nm) were observed in reflection spectra of CdGa2S4 crystals in crossed polarizers. This band has a half-width (HWHM) around ~3 - 5 Å. The birefringence interference are observed to the both sides of isotropic wavelength in reflection and transmission spectra. The isotropic wavelength for crystals grown by iodine transport method shifts to short-wavelengths (433 nm) in comparison with the crystals received by Bridgman method.

REFERENCES

[1] L.M. Suslikov, Z.P. Gadmashi, I.F. Kopinets, V.Ju. Slivka. Optics and Spectroscopy 50(4) (1973) 700-705.

[2] L.M. Suslikov, Z.P. Gadmashi, I.F. Kopinets, V.Ju. Slivka. Optics and Spectroscopy 51(2) (1981) 307-311.

[3] Ju.V. Vorosilov, V.Ju. Slivka, Anoxidic materials for electronic technics. Lvov, Viscaia Skola, (1989) 123. (in Russian)

[4] L.M. Suslicov, Z.P. Goldmasi, I.F. Kopinet, V.Ju. Slivka, Optics and Spectroscopy, 51 (1981) 307.

[5] L.M. Suslikov, V.Ju. Slivka, M.P. Lisita, Solid-state optical filters on hydrotropic crystals, Kiev, LTD, (1998) 1-194.

[6] I.G. Stamov, N.N. Syrbu, V.I. Parvan, V.V. Zalamai, I.M. Tiginyanu, Optics Communications, 309 (2013), 205-211.

[7] N.N. Syrbu, V.T. Tezlevan, Physica B, 210 (1995) 43.

[8] V.L. Panaiutin, B.E. Ponedelnikov, A.E. Rozenson, V.I. Chijikov, Izv. Vuzov SSSR, Fizika, 8 (1979) 57. (in Russian)

[9] V.L. Panaiutin, B.E. Ponedelnikov, A.E. Rozenson, V.I. Chijikov, Semiconductors, 15 (1981) 311.

[10] X. Jiang, W.R.L. Lambrecht, Phys. Rev. B, 69 (2004) 0352011.

[11] N.N. Syrbu, L.L. Nemerenco, V.Z. Cebotari, Crystal Res.&Technol., 37 (2002) 101.

[12] H. Neuman, W. Horig, G. Nooke, N.N. Syrbu, Solid State Communications, 65 (1988) 155.

[13] N.N. Syrbu, V.E. Tezlevan, V.I. Percicli, Optics and spectroscopy, 75 (1993) 355.

[14] H. Neuman, H. Sobotta, N.N. Syrbu, S.I. Radautsan, V. Riede, Crystal Res.&Technol., 19 (1984) 709.

[15] D. Erandonea, Ravhy S. Kumar, F.J. Manjon, V.V. Ursaki, I.M. Tiginyanu, Journal of Appl. Physics, 104 (2008) 063524.

[16] T.G. Kerimova, S.C. Mamadov, I.A. Mamedov, Semiconductors, 32 (1998) 148.

[17] A.N. Georgobiani, S.I. Radautsan, I.M. Tiginyanu, Semiconductors, 19(2) (1985) 193-212.

[18] A.N. Georgobiani, V.S. Donu, Z.P. Ilyuhina, Kr. soobsch. po fizike FIAN im. P.N. Lebedeva. 12 (1981) 48 - 52. (in Russian)

[19] A.N. Georgobiani, S.I. Radautzan, I.M. Tiginyanu, Phys. Status Solidi A, 69 (1982) 513 - 520.

[20] L.M. Suslikov, Z.P. Gadmashi, V.Yu. Slivka: Uzhgorodskiy gosunn-t (SSSR). - N3719803/24-10; 04.04.84; publ. 07.09.85, Byul. N 33. - 3 s. Optical filter A.S. 1177784 SSSR MKI 02 V 5/30.

[21] L.M. Suslikov, Z.P. Gadmashi, V.Yu. Slivka, Variable optical filters on the base of gyrotropic crystals with isotropic point. Optiko-meh. promyish. - 1988. - N3. - S.1-4. (in Russian)

[22] L.M. Suslikov, Z.P. Gadmashi, V.Yu. Slivka:A.S. 1283664 SSSR MKI 02 V 5/30. Opticheskiy filtr Uzhgorodskiy gosun-t (SSSR).; N3875689/24-10; Zayavl. 01.04.85; 0publ. 15.01.87, Byul. N2. - 4.

[23] V.V. Badikov, I.N. Matveev, S.M. Pshenichnikov Kvant-elektr. - 1981. - T.8, N4. - S.910-912.

[24] H. Sobbota, V. Riede, Wiss. Z. Karl-Marx_Univ. Leipzig, Math,-Naturviss. R., 20, (1971) 147-152.