ORDINARY AND EXTRAORDINARY DISPERSION IN ZnAs₂ AND CuGaS₂ CRYSTALS

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INTRODUCTION

The anisotropy of optical properties of crystals is known from the times when Fresnel discovered the birefringence phenomena in 1810. The difference between the propagation speed of lightwaves in different crystal's directions, Island spar and many other crystals has offered the possibility to develop optoelectronic devices with interesting properties. The anisotropy of optical properties in semiconductors is mainly researched for crystals of A_2B_6 group. The development of semiconductor crystals with a strong anisotropy of optical properties on which bases the development of *p-n* junctions' active elements, Schottky diodes is possible are of a big interest. The materials' properties which can be used in the near IR range (0.8–$1.5\mu m$) are especially interesting. Birefringent crystals are used in different polarization devices, interferometers, dispersion compensators, deflectors, channel splitters etc. Polarization states (i.e. the presence of ordinary and extraordinary rays) which create the difference of the effective paths' length for these polarization states determine the main application of such materials. Ordinary and extraordinary lightwaves which pass through such a crystal possess different levels of refraction and, respectively, obtain a different passage through the crystal. The last one determines great possibilities and wide application areas of these properties.

1. EXPERIMENTAL METHOD

The measurement of optical reflection and absorption spectra were taken at 10K and 300K temperatures at a high light power (1:2) spectrometer МДР-2 and at a double ray diffraction spectrometer JASCO-86.

2. EXPERIMENTAL RESULTS AND DISCUSSIONS

2.1. ZnAs₂ crystals

ZnAs₂ is a direct transitions semiconductor with a band-gap of *1.05eV* at *10K* temperature [1 –

4]. Boundary absorption at room temperature at $E||c$ and $E\perp c$ polarizations does not coincide [4 – 6]. The absorption at *1.35μm* wavelength at $E||c$ polarization is sharply increasing and the crystals with a thickness of some hundreds of microns become nontransparent. The crystals are transparent till the *1.3μm* wavelength at $E\perp c$ polarization. Sharp absorption margins with a maximum of *1.29μm* are observed at this wavelength and $E\perp c$ polarization. As the temperature decreases the absorption boundaries are shifting towards high energies. The temperature shift coefficient $\beta = \Delta E/\Delta T$ equals $3.1\times10^{-4}\ eV/rad$ for $E||c$ polarization and for $E\perp c$ polarization equals $4.6\times10^{-4}\ eV/rad$.

The interference of transparency and reflection spectra is observed in the transparency spectra of crystals with thin thicknesses $d \geq 25\ \mu m$. Figure 1 shows the transparency spectra of *ZnAs₂* single crystals with *22μm* obtained from gas phase and measured at *300K* for $E||c$ and $E\perp c$ polarizations, respectively.

An intensive Fabry-Perot interference is observed at both polarizations. The absorption is weaker at $E\perp c$ polarization than at $E||c$ polarization, this is why the interference spectra are revealed close to *1.3eV*. The oscillation amplitude in interference spectra decreases as the radiation energy is increasing.

The frequency dependence of the refractive index in the ω_0 region for a polarized oscillator can be determined by a mathematical equality of continuous oscillation with the damping factor. The frequency dependence of the refraction and absorption indexes can be determined by the dispersion correlations in a real crystal, which has several oscillators and several frequencies:

$$\begin{cases} n^2 + k^2 - 1 = \sum_{i=1}^{M} \dfrac{4\pi Ae^2}{m\varepsilon_0} \dfrac{\omega_{0i}^2 - \omega^2}{\left(\omega_{0i}^2 - \omega^2\right)^2 + \gamma^2\omega^2} = \varepsilon_1 \\[4mm] 2nk = \sum_{i=1}^{M} \dfrac{4\pi Ae^2}{m\varepsilon_0} \dfrac{k^2\omega^2}{\left(\omega_{0i}^2 - \omega^2\right)^2 + \gamma^2\omega^2} = \varepsilon_2 \end{cases} \quad (1)$$
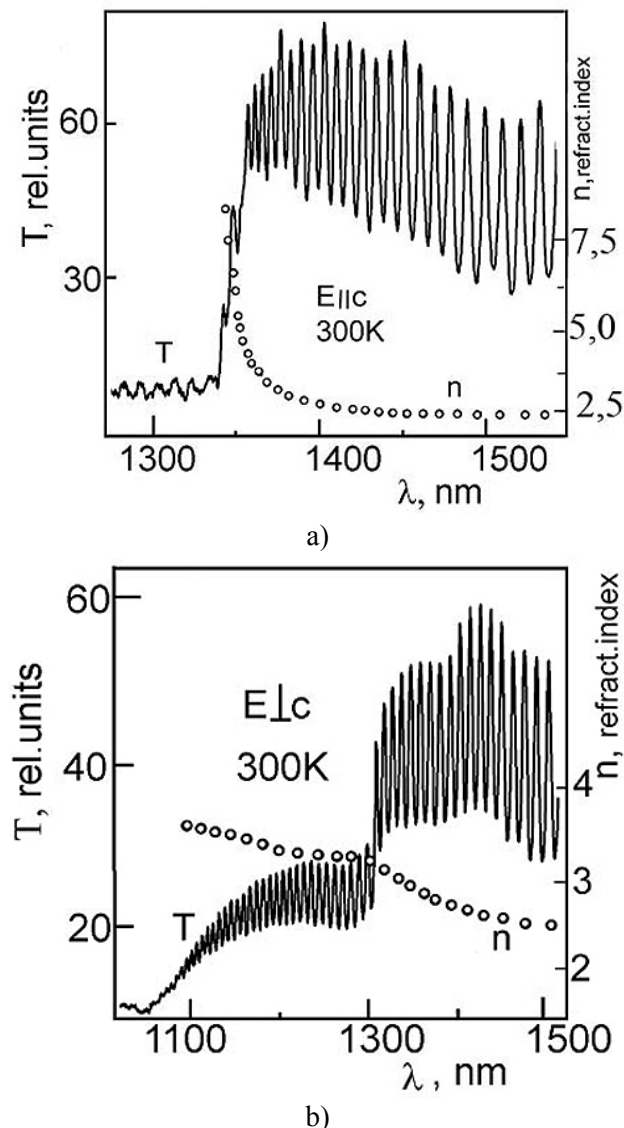
The spectral dependencies n, k, ε_1 and ε_2 in the region of crystals' transparency ($k << n$) are calculated from the experimentally measured transparency spectra. This method is extremely productive in case of interference spectra measurements for thin crystals. In the region of $E > E_g$ energies the materials are not transparent and the calculation method of these parameters by the Kramers-Kronig relations from reflection spectra is used to determine n, k, ε_1 and ε_2. Interference absorption (reflection) spectra contain maxima and minima corresponding to the following expressions:

a)

b)

Figure 1. *a)* The transparency interference spectra of thin ZnAs₂ crystals (thickness $d = 22\mu m$) at E‖c and E⊥c polarizations and 300K temperature; *b)* Spectral dependence of the refractive index obtained from the interference of transparency spectra calculations.

$$\lambda_{\max} = \frac{2nd}{m_1}; m_1 = 2,4,6 \qquad (2)$$

$$\lambda_{\min} = \frac{2nd}{m_2}; m_2 = 1,3,7 \qquad (3)$$

where: $\lambda_{\max}, \lambda_{\min}$ – maxima and minima wavelengths in interference spectra, n – refractive index, m – order of interference strip, d – crystal's thickness. The refractive index for two adjacent strips is determined by the expression:

$$n = \frac{1}{2d\left(\dfrac{1}{\lambda_1} - \dfrac{1}{\lambda_2}\right)}. \qquad (4)$$

The obtained spectra show that the distances between peaks (minima) are practically faintly changing as the energy increases at $E\perp c$ polarization. The refractive indexes for lightwaves with $E\perp c$ polarization in the wavelength range *1100 – 1500nm* is changing from *2.51* up to *3.71*. The maxima (minima) of interference spectra show inspissations at $E‖c$ polarization, i.e the distances between them is shortening while approaching to the resonant frequency of the electronic transition. The value of the refractive index changes form *2.7* up to *7.0* in the region *1500 – 1350nm* at $E‖c$ polarization (at some samples the maximal value reached *8.1*). The growth of the refractive index as the energy of the lightwave increases reflects the branch of the ordinary dispersion. Weak strips that are residual from the $E\perp c$ polarization are observed in the energy region $E > 1.04eV$ at $E‖c$ polarization. The following thicknesses of *ZnAs₂* for $E‖c$ wave lengths are nontransparent and, respectively, the interference spectra must not be revealed. The obtained values of the refractive index at $E‖c$ polarization are practically proving the frequency dependence of the polaritonic branch in the "bottle-neck" region discussed in the works [5, 6]. The discussed anisotropy of optical properties and the dispersion of refractive index of ordinary and extraordinary rays in *ZnAs₂* are intrinsic properties of this material. This anisotropy is also observed for thin crystals (several microns) [5, 6].

Figure 2 shows the transparency interference spectra of *ZnAs₂* crystals at $E‖c$ and $E\perp c$ polarizations and *22K* temperature. A thin Fabry-Perot interference structure is observed at both polarizations. The transparency reaches the minimal energy value *1.0306eV* at $E‖c$ polarization, this value corresponds to the minimal energetic distance between $V_1 - C_1$ zones. The common contour of transparency spectra at $E\perp c$ polarization repeats the

a)

b)
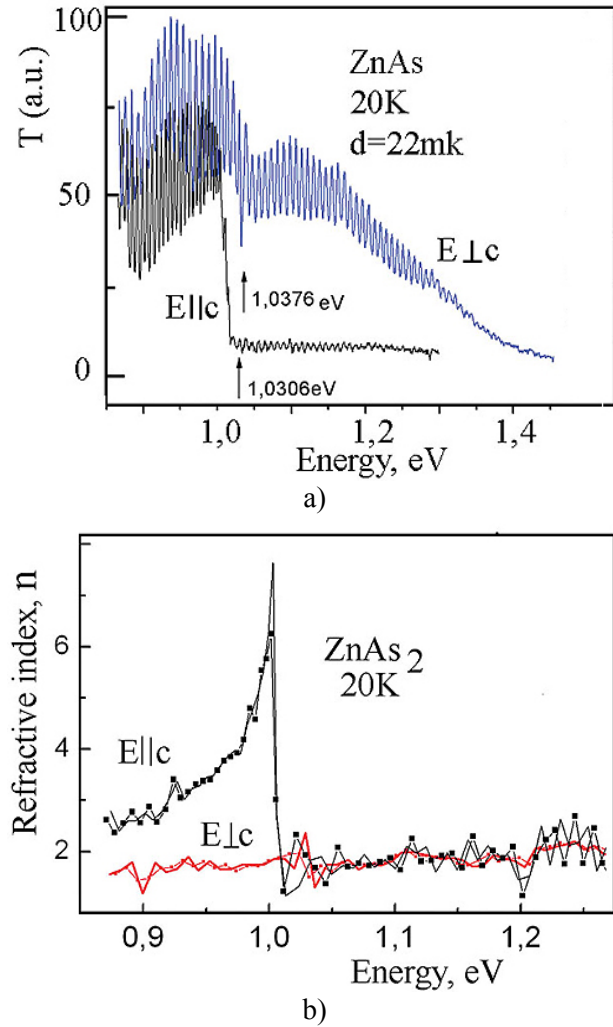
Figure 2. *a)* Transparency interference spectra; *b)* Spectral dependence of the refractive index of ZnAs₂ crystals at 22K temperature.

transparency spectra contour at the given polarization for thicker thicknesses (*fig. 2*). A pronounced interference up to *1.3eV* is revealed in spectra. A minimum in the interference spectra at *1.0376eV* energy occurs in the region of direct transitions at the given polarization. This value corresponds to the direct transition in $k = 0$. The calculations of the refractive index at both polarizations are shown in figure 2. As it is evident from the figure the refractive index is obtained as in the ordinary dispersion region as in the extraordinary one.

The intersection phenomenon of dispersion curves n_e and n_o is observed at crystals because as the lightwave energy value decreases from the minimum of the band-gap the character of the electronic transitions changes. At some wavelength the ordinary and extraordinary waves are phase matching. If the phase matching condition is approved in the crystal, then the energy transfer can be realized from one mode to another, polarized

orthogonally to the first one. As the distance from the absorption boundary increases towards long wavelengths' region the absorption value at $E||c$ polarization decreases sharply, than the absorption at $E\perp c$ polarization. At some wavelength λ_0 the absorption curves and, respectively, the *n* curves are intersecting. The energy transfer from the mode polarized as n_0 (or n_e) to the mode polarized as n_e (or n_0) occurs while the radiation with the $\lambda = \lambda_0$ wavelength passes through the crystal, i.e. the interaction of two orthogonally polarized modes is observed in the isotropic point (IP) of the crystal.
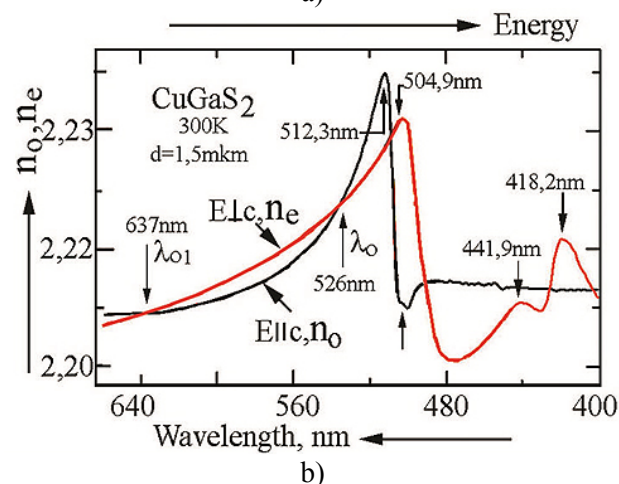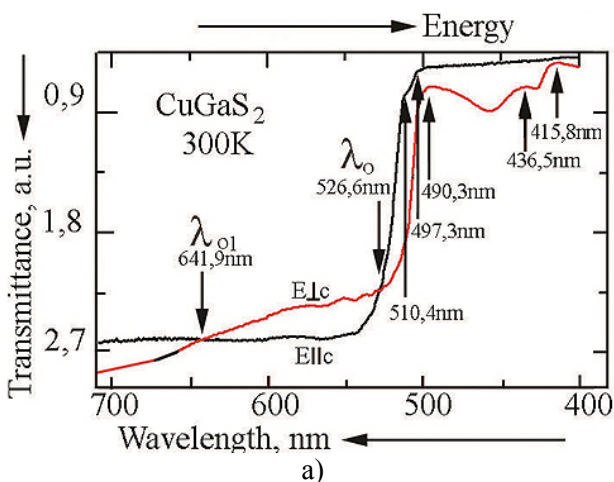
2.2. CuGaS₂ crystals

Two particularities, *a* and *b*, at *510.4nm* (*2.428eV*) and *493.7nm* (*2.511eV*) are revealed at room temperature at *CuGaS₂* crystals for $E||c$ polarization in the transparency spectra. These particularities are conditioned by the electronic transitions $\Gamma_7(V_6) - \Gamma_6(C_1)$ and $\Gamma_7(V_2) - \Gamma_6(C_1)$ from the valence zones to the conduction zones, respectively, (*fig. 3*) [7 – 9]. A particularity at 490.3nm (2.528eV) is observed at $E\perp c$ polarization, which is conditioned by the electronic transitions $\Gamma_6(V_3) - \Gamma_6(C_1)$. It is evident from this data that the energetic interval between the zones $V_1 - V_2$ equals *83meV* and between $V_2 - V_3$ equals *17meV*.

These results prove that the energetic intervals between valence zones at room temperature are different from these intervals at *10K* [7 – 9]. In addition, the symmetry of V_2 zone became Γ_7 and the one for V_3 zone became Γ_6. The symmetry of these zones is inversed at *10K*. Consequently, as the temperature decreases different temperature coefficients of V_2 and V_3 zones' shift lead to the fact that those ones change their positions. The transparency curves are intersecting in the region *600 – 650nm*, which gives evidence on the presence of the isotropic point (*fig. 4*). Figure 4 shows the transparency spectra for crystals with *4.5μm* thickness at $E||c$ and $E\perp c$ polarizations. It is evident from the figure that the curves of the transparency spectra are intersecting in the region *641.9nm* (λ_{01}) and in the region *526.6nm* (λ_0). The calculation of the refractive indexes n_o ($E||c$) for the ordinary and n_e ($E\perp c$) for extraordinary rays had proved the presence of isotropic wavelengths at *637nm* and *526nm*. The optical constants *n*, *k*, ε_1 and ε_2 are calculated (*fig. 5*, right part) for these crystals in the particularities' region linked with the optical transitions in the band-gap minimum (wavelengths region *560 – 400nm*).
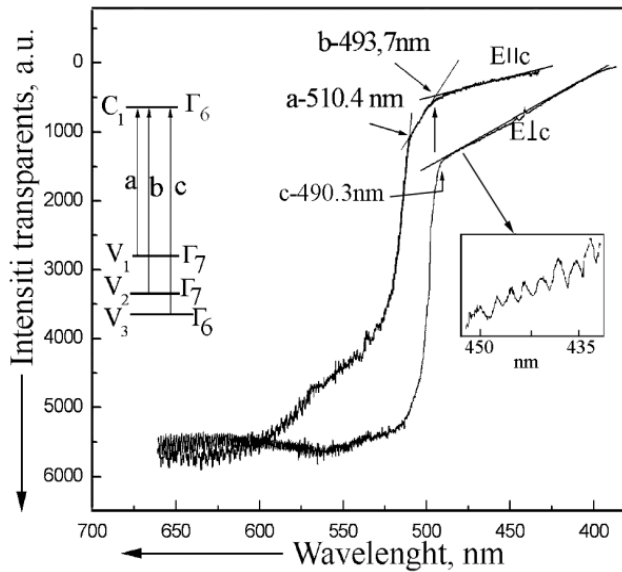
Figure 3. Transparency spectra of CuGaAs$_2$ crystals with 14.5μm thickness at 300K and E||c, E⊥c polarizations.
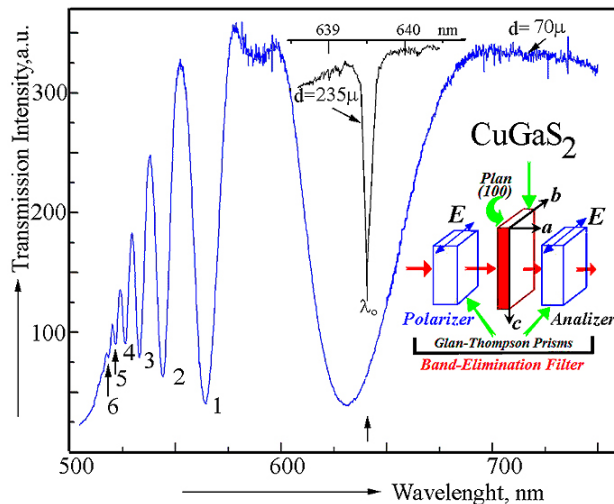

Figure 4. *a)* Transparency spectra of CuGaAs$_2$ crystals with 4.5μm thickness at 300K and E||c, E⊥c polarization; *b)* Spectral dependence for ordinary n$_o$ (E||c) and extraordinary n$_e$ (E⊥c) rays (crystals' thickness 4.5μm).
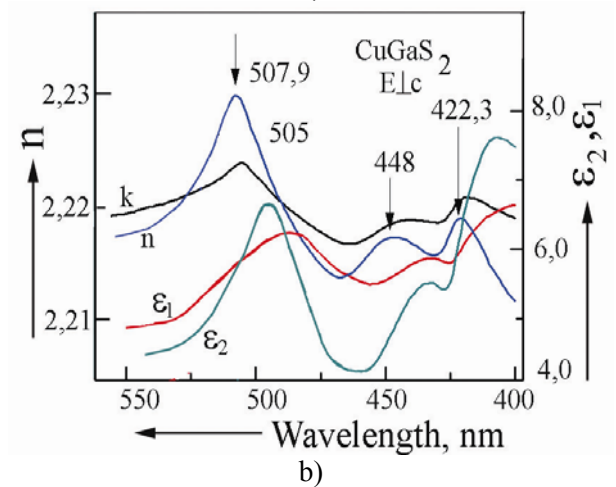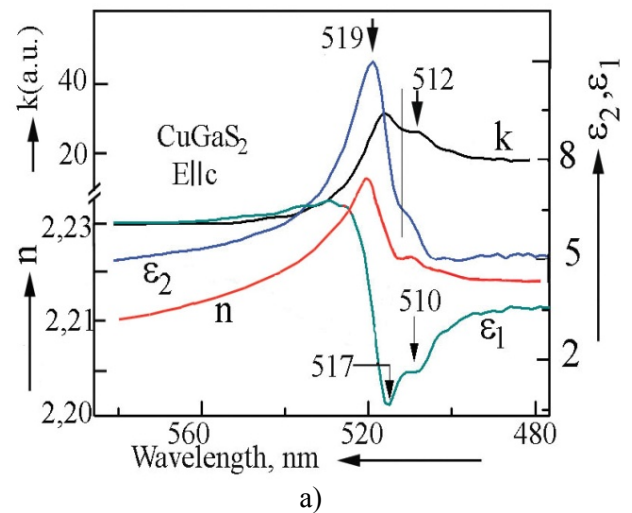
Figure 5. *a)* Spectral dependence of n$_o$, n$_e$, k, ε$_1$ and ε$_2$ for the ordinary rays (E||c) at CuGaS$_2$ crystals; *b)* Spectral dependence of n$_o$, n$_e$, k, ε$_1$ and ε$_2$ for the extraordinary (E⊥c) rays at CuGaS$_2$ crystals; (crystals' thickness 4.5μm).

The transparency spectra of a plane-parallel plate of a certain thickness (*0.007mm* and *0.235mm*) positioned between two polarizators parallel oriented are shown in figure 6. The optical axis of the crystal is positioned in the plate's plane. A thin absorption line at *639.5nm* is observed for these crystals' thicknesses. This structure represents a *Band Elimination Filter*. Thin lines 1 – 6 which distance between deepens towards short wavelength part are revealed from the short wavelength part λ_0 at crystals with thin thicknesses (0.007mm).

The dispersion is determined by the hypotrophy properties of the crystal lattice from the long wavelength part of λ_0 that leads to negative birefringence ($-\Delta n = n_e - n_o$, the refraction index for ordinary n_o and extraordinary n_e rays). A contribution to the negative birefringence can also make the deformational lattice distortions $|(1 - c/2a)|$,

Figure 6. Transparency spectra of CuGaS$_2$ crystals positioned between parallel oriented polarizators (Band Elimination Filter).

where *c* and *a* are the lattice parameters. The negative birefringence can be also linked with other mechanisms, for example, the anisotropy of impurities absorption, free charge carriers etc. Birefringence $(-\Delta n)$ is a crystals' property at the crystals measured by us and is not an induced one.

1. CONCLUSIONS

In conclusion is has to be mentioned that such materials can be used as comb filters in the visible and near IR range and all birefringent crystals can be successfully used for developing different polarization devices, interferometers, dispersion compensators, deflectors, channel splitters etc.

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