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OPTICAL PROPERTIES OF $HgGaInS_4$ CRYSTALS

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Abstract. Luminescence, transmission, reflection, and wavelength modulation transmission and wavelength modulation reflection spectra of $HgGaInS_4$ crystals were researched in the temperature range of 300-10 K. This article discusses the various features observed in the spectra of $HgGaInS_4$ crystals. The dependence on temperature of the energy gap is shown. Spectra of wavelength modulation transmission have minima a_1, a_2, and a_3, which vary with temperature and are caused by indirect transitions L-Γ with phonon absorption and emission. Spectra of thicker crystals have more features caused by the same indirect transitions. The photoluminescence show a strong maximum at 2.43 eV, attributed to radiative recombination of free excitons. These various features have significant implications for the understanding of the electronic and optical properties of $HgGaInS_4$ crystals.

Keywords: *Photouminescence, transmission, reflection, wavelength modulation transmission and reflection, absorption, emission.*

Rezumat. Au fost cercetate spectrele de luminescență, de transmisie, de reflexie și modulate în funcție de lungimea de undă a transmisiei și reflexiei ale cristalelor $HgGaInS_4$ în intervalul de temperatură 300-10 K. În acest articol se discută diferite caracteristici observate în spectrele cristalelor $HgGaInS_4$. Este prezentată dependența de temperatură a energiei de bandă. Spectrele de modificare a transmisiei în funcție de lungimea undei, cu minime a_1, a_2 și a_3, care variază cu temperatura și sunt cauzate de tranziții indirecte L-Γ cu absorbție și emisie de fononi. Spectrele cristalelor mai groase au mai multe caracteristici cauzate de aceleași tranziții indirecte. Spectrele de fotoluminescență arată un maxim puternic la 2.43 eV, atribuit recombinării radiative a excitonilor liberi. Aceste diferite caracteristici au implicări semnificative pentru înțelegerea proprietăților electronice și optice ale cristalelor $HgGaInS_4$.

Cuvinte cheie: *Luminescență, transmisie, reflexie, transmisie și reflexie modulate în funcție de lungimea de undă, absorbție, emisie.*

1. Introduction

Crystals $HgGaInS_4$ formed when defect chalcopyrite $HgGa_2S_4$ interacts with spinel $HgIn_2S_4$ and has layered structure. The lattice structure of $HgGaInS_4$ crystals consists of an arrangement of anions in a hexagonal close-packed structure, with layers of cations occupying particular arrangement both voids in the shape of tetrahedrons and octahedrons [1].

The hexagonal lattice of $HgGaInS_4$ crystals has unit cell parameters (lengths of the cell edges) of a = b = 0.39 nm and c = 3.14 nm [1]. $HgGaInS_4$ crystals exhibit similar chemical, crystalline and electrophysical properties compared to $ZnIn_2S_4$, $CdGaInS_4$, $CdIn_2S_2Se_2$ crystals [2].

The highly pronounced layered structure of $ZnIn_2S_4$ crystals, which belong to the $A^{II}B_2^{III}C_4^{VI}$ group of ternary semiconducting compounds, makes them particularly interesting and has attracted the attention of researchers, leading to numerous experimental studies [3-4]. These crystals possess photo-sensitivity and exhibit photoluminescence [5-6], showcasing intriguing optical properties.

The classic thiospinel structure is the crystalline form of $HgIn_2S_4$ compounds. The optical properties of compounds in this group have been predominantly studied using crystals like $ZnIn_2S_4$, $ZnAl_2Se_4$, and $CdGa_2S_4$ [7-13]. These crystals are utilized in various optical filters and nonlinear optical devices. Investigated materials such as $HgIn_2S_4$ and $HgGa_2Se_4$ are intriguing due to their linear and nonlinear optical characteristics, as well as their narrow band gap of 1.2-1.6 eV [9,14].

2. Materials and Methods

The single crystals of $HgGaInS_4$ were grown by the gas transport method in ampoules. The material was grown with mirror-like surfaces with dimensions of ~10x7 mm^2. The plates had different thicknesses (0.01-3 mm) and were easily cleavable. Monocrystals of nanoscale thickness (50 nm) were visually distinguishable by their color. The spectra at low temperatures of the material placed in a helium cryostat LTS-22 C 330 cryogenic optical system were obtained using an MDR-2 spectrometer with an aperture with a ratio of 1:2 and a linear dispersion of 0.7 nm/mm. The optical system of the MDR-2 spectrometer is shown in Figure 1.

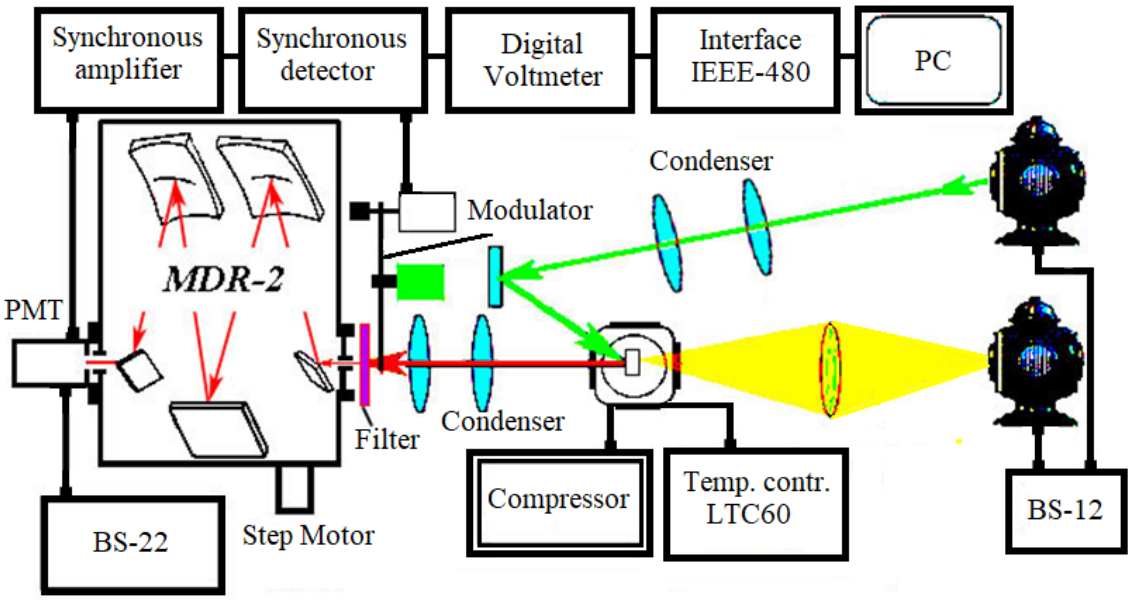


Figure 1. Schematic representation of set-up based on single spectrometer MDR-2 for transmission and reflection spectra registration.

The photoluminescence spectra were measured using the double-beam spectrophotometer SDL-1 with a light amplification ratio of 1:2 and a linear dispersion of 0.7 nm/mm. The optical system of SDL-1 is shown in Figure 2.

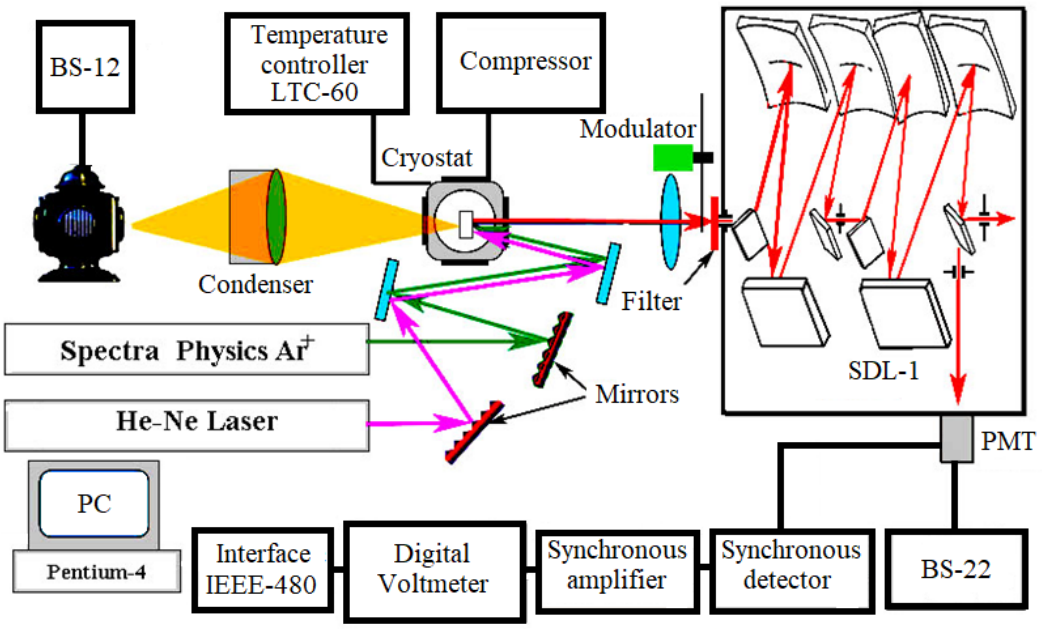


Figure 2. Scheme of measurement installation based on double spectrometer SDL-1 for photoluminescence spectra registration.

3. Results

Initial results on the absorption and photoluminescence of $HgGaInS_4$ crystals have been previously investigated [2]. The energy gap of $HgGaInS_4$ is equal to 2.41 eV at temperature 300 K and 2.46 eV at 80 K [2]. It was also noted that the exponential tail of the absorption edge is caused by the existence of states that are distributed quasi-continuously [15].

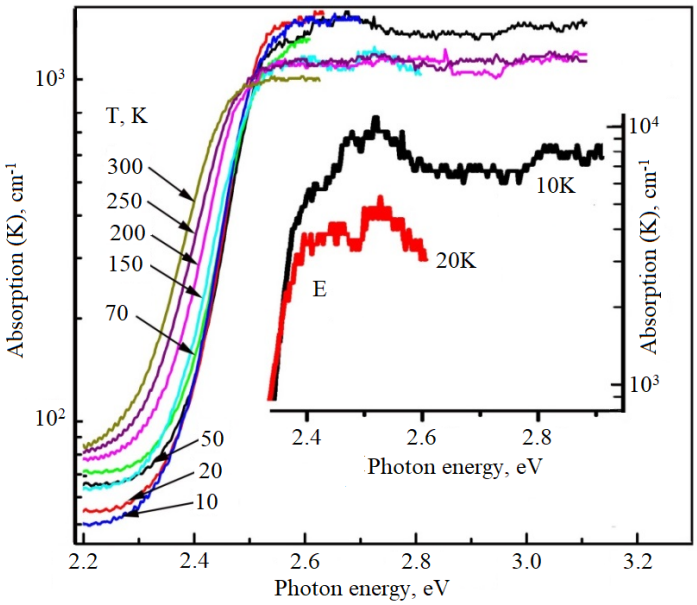
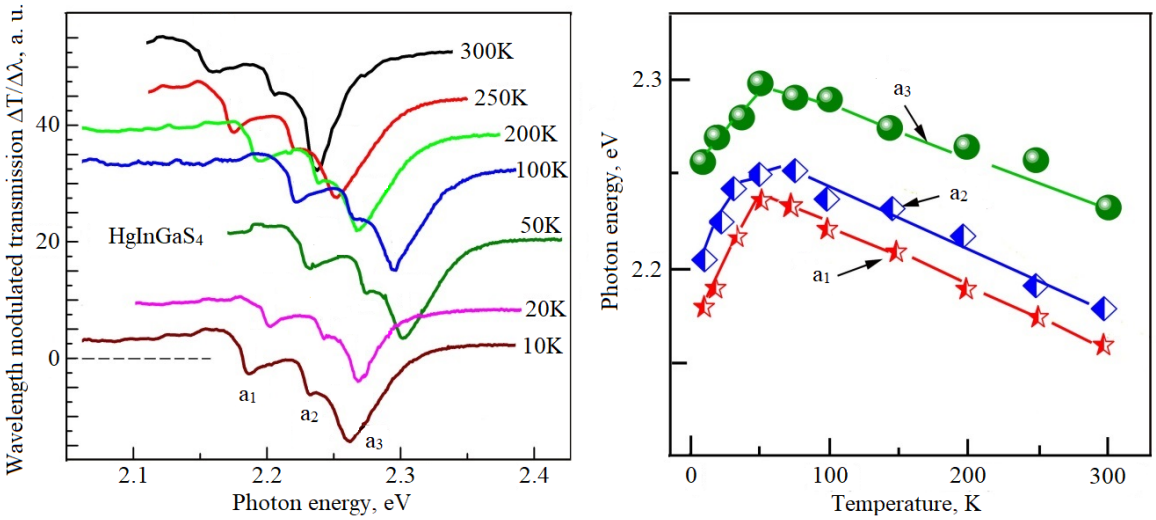


Figure 3. Absorption edge of $HgGaInS_4$ crystals, with thicknesses 0.1-0.6 μm within the temperature interval of 300-10 K and with a thickness of 1.2 μm (insert).

The newly discovered layered phase of $HgGaInS_4$ has a crystalline structure that includes empty spaces or vacancies within the cation lattice and the atoms in the cation sublattice are randomly distributed. This material is an electron semiconductor, with a band gap of 2.41 eV, high sensitivity to light, strong photoluminescence. In the band gap, there are exponentially distributed electron traps (with a characteristic energy of about 65 meV) near the conduction band bottom, and several distinct energy levels positioned roughly at 0.01, 0.11, and 0.2 eV above the top of the valence band. The initial two levels are associated with radiative electron transitions from donor-like states that are exponentially distributed. The third level is a sensitizing level. The slope of electron transitions from the valence band to quasi-

continuously distributed states in the exponential region of the absorption edge remains constant regardless of temperature.

Figure 3 shows the spectra of absorption of $HgGaInS_4$ thicknesses of crystals 0.1-0.6 μm at different temperatures in the interval of 300-10 K. Decreasing temperature leads to the absorption edge shifts towards higher energies. Measurements were conducted also on crystals with thicknesses of 1-1.2 μm in the range where absorption coefficients are higher than 10^3 cm^{-1} (see insert from Figure 3). Maxima can be detected on the spectra at energies of 2.42-2.53 eV.



a) b)

Figure 4. Temperature dependence of wavelength modulation transmission (ΔT/Δλ) (a) and of a_1, a_2 and a_3 minima positions (b).

The spectra of the wavelength modulation transmission change ΔT/Δλ of $HgGaInS_4$ crystals at temperatures of 10-300K exhibit features (minima) a_1, a_2, and a_3, the energy positions of which vary with temperature, as shown in Figure 4a and Figure 4b, positions of peaks is shown in table 1.

Table 1

Temperature values and peak positions used in the research

Temperature, K	Peak position, eV
10	a_1 – 2.188
	a_2 – 2.231
	a_3 – 2.261
20	a_1 – 2.191
	a_2 – 2.242
	a_3 – 2.269
50	a_1 – 2.232
	a_2 – 2.273
	a_3 – 2.303
100	a_1 – 2.222
	a_2 – 2.267
	a_3 – 2.295
200	a_1 – 2.193
	a_2 – 2.241

Continuation Table 1

	a_3 – 2.269
250	a_1 – 2.175
	a_2 – 2.224
	a_3 – 2.252
300	a_1 – 2.161
	a_2 – 2.206
	a_3 – 2.237

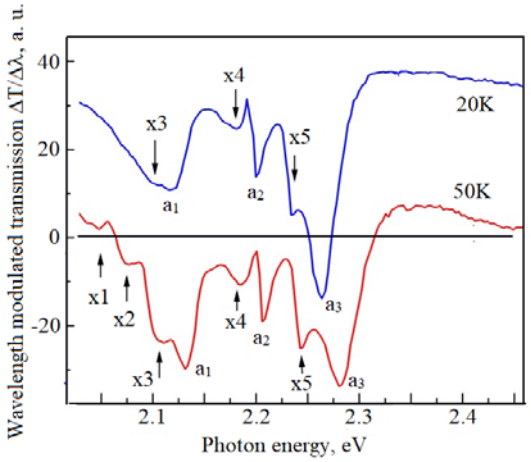


Figure 5. Spectra of wavelength modulation transmission (ΔT/Δλ) for $HgGaInS_4$ crystals with a thickness of 600μm at temperatures of 20 and 50K.

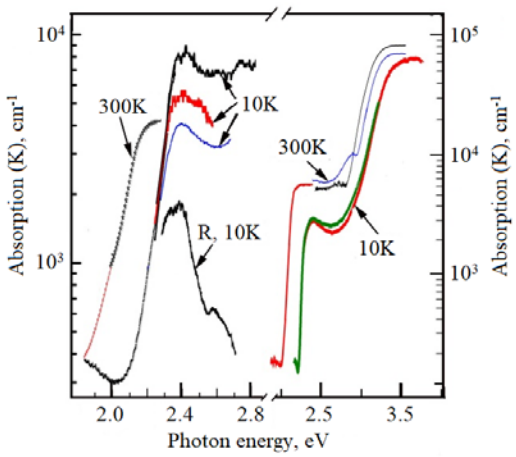


Figure 6. Spectra of absorption (K) of $HgGaInS_4$ with different thicknesses (right side – 0.5mm, left side - 0.1mm), at temperatures of 10 K and 300 K.

On the other hand, massive crystals with thickness about (600 μm) exhibit minima x1-x5, as shown in Figure 5. We assume that x1-x5 and a_1-a_3 are caused by indirect transitions L-Γ (E_g^{ind}-2.2-2.3 eV) with phonon absorption and emission. Thicker crystals and additional investigations are required for a more accurate determination of this interval.

Figure 6 shows the shift of the absorption edge spectra of $HgGaInS_4$ crystals with a thickness of 0.5 mm in the temperature interval of 300-10 K. As seen from the spectra, at temperature 300K the absorption edge starts at 1.9 eV, at temperature 10 K, at 2.08 eV. At an absorption coefficient of 10^3 cm^{-1}, the temperature coefficient of the absorption edge shift (ΔEg/ΔT) equal to $8.1 \cdot 10^{-4}$ eV/K. Decreasing temperature leads to a shift of the absorption edge towards higher energies. At absorption coefficients of $3 \cdot 10^3$ cm^{-1}, coefficient of the temperature shift of the absorption edge (ΔEg/ΔT) is $6 \cdot 10^{-4}$ eV/K, and at an absorption coefficient of $3 \cdot 10^4$ cm^{-1}, *β*(ΔEg/ΔT) is twice as small and equal to $-3 \cdot 10^{-4}$ eV/K. These data practically confirm the concept that changes in temperature have a weaker effect on deep energy levels and high-energy electronic transitions.

Figure 7 shows the reflection spectra of 0.5 mm thick $HgGaInS_4$ crystals at temperature 10 K in the high absorption region. In the energy interval of 2.4-2.6 eV, a weak change in reflection spectra is observed with a maximum at 2.4 eV. The change in intensity from the maximum to the minimum occurs within 6-7%. This characteristic is more clearly distinguished in the reflection spectra wavelength modulation. The observed R feature is due to direct electronic transitions into the exciton zone at the Γ point.

Measured excitonic reflection ($R_{exper.}$) and calculated using a one-oscillator model ($R_{calc.}$) spectra is presented in Figure 5.

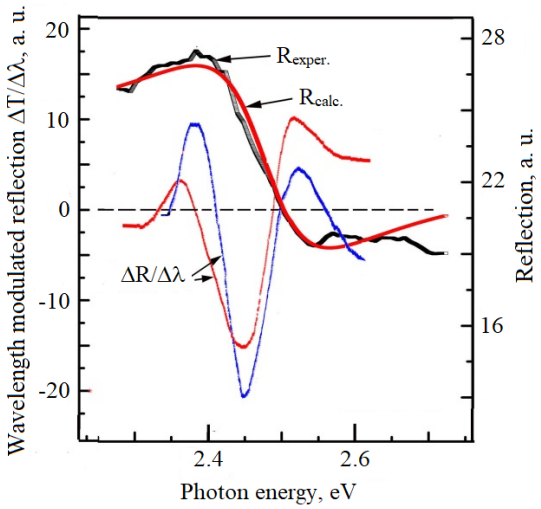


Figure 7. Reflection spectra and spectra of wavelength modulation reflection (ΔR/Δλ) of $HgGaInS_4$ crystals with a thickness of 0.5mm at temperature 10K.

The resonant value of the excitonic transition is 2.43 eV, the background dielectric constant is 9.83, the splitting between longitudinal and transverse components is 13 meV, and the factor of damping is about 187. Naturally, with such a large damping factor, the excitonic reflection spectra contour is weakly distinguished.

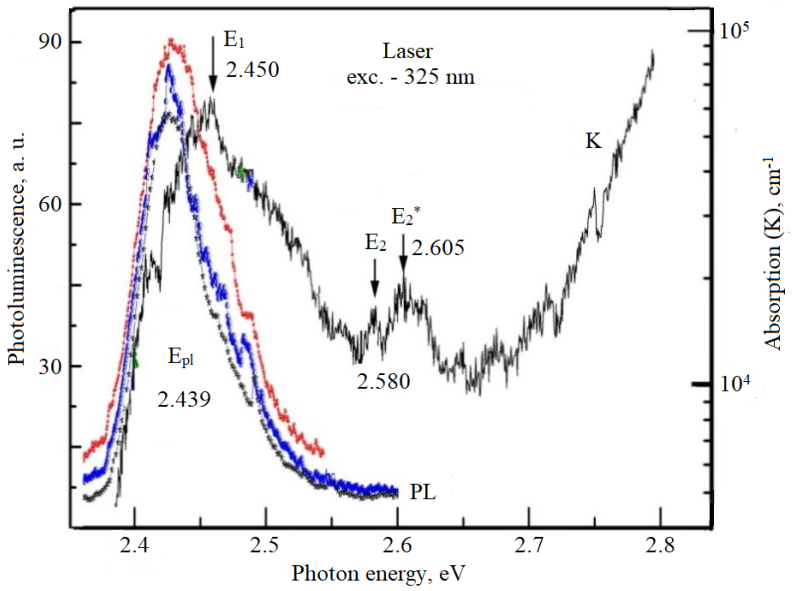


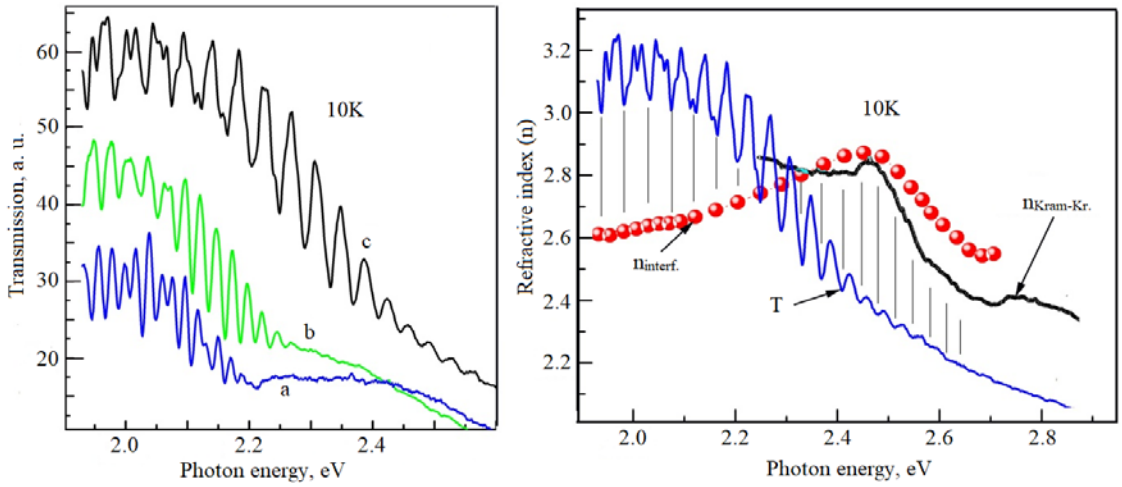
Figure 8. Absorption spectra of $HgGaInS_4$ crystals with a thickness of 0.1 μm and photoluminescence spectra with excitation wavelength 325 nm laser at 10 K.

Absorption spectra of crystals with a thickness of 0.1 μm clearly show peaks at E_1 (2.450 eV), E_2 (2.580 eV), and E_2^* (2.605 eV), as shown in Figure 8. The photoluminescence spectral dependence of $HgGaInS_4$ crystals with excitation wavelength 325 nm at temperatures of 20 K and 10 K shows an intense peak at 2.439 eV, as can be seen Figure 8. The comparison of the absorption and photoluminescence peaks suggests that the E_1 absorption peak and E_{PL} photoluminescence peak are associated with the excitonic transition. The E_2 and E_2^* absorption peaks are associated with the n=2 and n=3 states, respectively. In this case, the exciton binding energy (Rydberg constant) is 180 meV, and the bandgap width is 2.619 eV.

The interference fringes are clearly visible in the spectra, and as can be seen, the interference spectra extend more into the short-wavelength region as the crystals become thinner. The refractive index was determined by using the relation between the energy positions of the observed maxima (or minima) and the refractive index:

$$\boldsymbol{n} = \frac{\boldsymbol{M}}{2\boldsymbol{d}\left(\frac{\boldsymbol{1}}{\boldsymbol{\lambda_1}} - \frac{\boldsymbol{1}}{\boldsymbol{\lambda_2}}\right)} \quad , \tag{1}$$

M equal to 1 for nearby maxima (minima); $\boldsymbol{\lambda_1}$ and $\boldsymbol{\lambda_2}$ position value (nm) for maxima (minima) in interference spectra.



a) b)

Figure 9. Transmission spectra of crystals with different thicknesses (a-270 μm, b-120 μm, c-0.1 μm) at 10 K (a). Dependence of the refractive index n(interf.) calculated from interference transmission spectra (T) and from the Kramers-Kronig calculation of the reflection spectra (n-Kram-Kr) (b).

The spectral dependence of the refractive index $n_{interf.}$ obtained from the calculation of interference transmission spectra (T) is presented in Figure 9b. The obtained spectra are compared with the refractive index spectral dependence $n_{Kram-Kr.}$ obtained through calculations of the reflection spectra R applying the Kramers-Kronig equation. The spectral dependences of the reflection coefficient (R) and the optical constants refractive index (n), extinction coefficient (k), real part of permittivity (ε_1), imaginary part of permittivity (ε_2), and phase (ϕ) are interconnected by Kramers-Kronig relationships. These relationships allow the calculation of one parameter from another and are useful in analyzing the optical properties of materials.

$$\begin{cases} r = \dfrac{N-1}{N+1} = \dfrac{n+ik-1}{n+ik+1} \\ r = \sqrt{R}e^{-i\varphi} = \sqrt{R}\left(\cos\varphi - i\sin\varphi\right) \end{cases} \Rightarrow \begin{cases} n = \dfrac{1-R}{1-2\sqrt{R}\cos\varphi + R} \\ k = \dfrac{2\sqrt{R}\sin\varphi}{1-2\sqrt{R}\cos\varphi + R} \end{cases} \tag{2}$$

As can be seen, the refractive index values and the spectral dependence obtained by the two methods are in good agreement.

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4. Discussion

The study of the $HgGaInS_4$ crystals revealed interesting properties related to their optical absorption, reflection, and transmission spectra. The absorption edge of the material shifts towards higher energies as the temperature decreases, indicating that the temperature has a lesser effect on deep energy levels and high-energy electronic transitions [1]. The thickness of the crystal affects the appearance of features in the absorption spectra, which may be caused by indirect transitions with phonon absorption and emission [16].

The reflection spectra of the crystals exhibit a weak change in the intensity in the energy interval of 2.4-2.6 eV, with a maximum at 2.43 eV, which is attributed to direct electronic transitions into the exciton zone at the Γ point. The photoluminescence spectra also show peaks related to exciton modes [16].

The transmission spectra exhibit interference fringes that extend more into the short-wavelength region as the crystals become thinner, and the refractive index values obtained by the two methods (refractive index obtained from the calculation of interference spectra and obtained through calculations applying Kramers-Kronig equation) are in good agreement.

Overall, the study of the $HgGaInS_4$ crystals provided valuable insights into the optical properties of the material, which could be useful for applications in optoelectronics and photonics. Further investigations on the material's properties, particularly on thicker crystals, are required for a more accurate determination of the observed features and transitions.

5. Conclusions

The study of $HgGaInS_4$ crystals' spectra has revealed several significant features. The shift in the absorption edge towards higher energies with decreasing temperature indicates a temperature dependence of the bandgap energy. The wavelength modulation transmission spectra exhibit energy minima caused by indirect transitions L-Γ with phonon absorption and emission, and the spectra of thicker crystals have additional minima due to the same transitions. The weak change in the reflection spectra at energies between 2.4-2.6 eV, with a maximum at 2.4 eV, is resulted by direct electronic transitions to excitonic zone at the Γ point. Spectra of photoluminescence with an excitation by a 325 nm show a strong maximum at 2.21 eV, resulting from the radiative recombination of free excitons. The absorption edge temperature shift coefficient varies with the absorption coefficient, indicating that temperature changes affect deep energy levels and high-energy electronic transitions to a lesser extent. Overall, these results provide valuable insights into the electronic and optical properties of $HgGaInS_4$ crystals.

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Conflicts of Interest: The author declares no conflict of interest.

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