Birefringence in $ZnIn_2S_4$ layered crystals

V.V. Zalamai
Technical University of Moldova,
Chisinau, Republic of Moldova

E.V. Rusu
Institute of the Electronic Engineering and Nanotechnologies "D. Ghitu",
Chisinau, Republic of Moldova

A.V. Tiron
Technical University of Moldova,
Chisinau, Republic of Moldova

N.N. Syrbu
Technical University of Moldova,
Chisinau, Republic of Moldova

***Abstract* - Interference spectra of $ZnIn_2S_4$ crystals by 7.5 - 900 μm thicknesses were investigated. Spectral dependences of refractive indices (n_o and n_e) were calculated and they intersection was observed at energy E_0 ~ 2.8 eV. The spectral dependence $\Delta n = n_o - n_e$ at energy region 0.8 - 3.0 eV was determined.**

***Index Terms* – layered crysatls; birefringence; interference spectra; ordinary and extraordinary waves; isotropic wavelength;**

I. Introduction

$ZnIn_2S_4$ crystals belong to triple semiconductor compounds $A^{II}B_2^{III}C_4^{VI}$ and attract an interest due to a well pronounced layered structure. This feature attracts an attention of scientists and stimulates experimental investigations [1]. The crystals are photosensitive and luminescent and possess interesting optical properties [2]. Of particular interest is the fact that this compound is formed in the form of various crystalline polytypes (α, β and γ) [3]. Crystals are of interest from a technological point of view. It was shown a possibility of receiving of thin nono-layers by chemical methods [4]. Understanding of optical, photoelectrical and luminescent properties of these materials are available after electron band structure calculation of these crystals [5].

II. Experimental methods

$ZnIn_2S_4$ single-crystals were grown by the method of transferring components from the gas phase. The obtained crystals had dimensions of 2x2 cm and a thickness of 1 mm to a fraction of microns. The crystals of R_{3m}-C_{3v}^5 symmetry are red-yellow plates and have been ascribed to ***α***-polytyps. Another type of crystals has similar sizes but a lighter yellow color and these crystals have been attributed to R_{3m}-D_{3d}^5 symmetry (polytype ***γ***) and R_{3m}^1-C_{3v}^1 symmetry (polytype ***β***) [5]. The monocrytals structure and they parameters were controlled by x-ray diffraction methods. 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

$ZnIn_2S_4$ crystals are an amazing object for optical transmission (absorption) spectra measurements since they are layered with weak bonds between layers. This weak bond between layers allows to receive from gas phase a very thin plates with thicknesses around tens of nanometers.

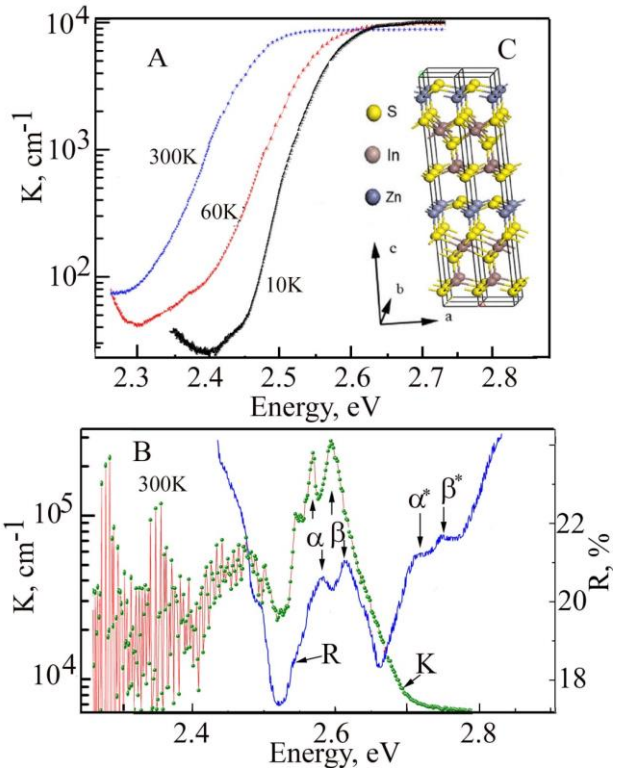

Fig. 1 Absorption (K) and reflection (R) spectra measured at temperatures 10K, 60 K and 300 K (A and B) and unit cell of crystal structure of $ZnIn_2S_4$ ***α*** polytype of C_{3v}^5 symmetry (C).

Figure 1, A shows absorption spectra (K) of $ZnIn_2S_4$ crystals of different thicknesses (***d*** ~ 50 - 900 μm) measured at temperatures 10, 60 and 300 K and also a fragment of layers of crystal formed a unit cell and directions of ***a***, ***b*** and ***c*** axes. An

absorption edge shift temperature coefficient is equal to 0.02 eV/K. Figure 1, B shows absorption spectra (K) of 67 μm crystal and reflection spectra (R) of 845 μm thickness crystal at room temperature. A well pronounced interference is observed at energies less than 2.5 eV. Five bands (***α*** - 2.567 eV, ***β*** - 2.598 eV, ***α**** - 2.728 eV, ***β**** - 2.765 eV and γ - 2.864 eV) were observed in absorption spectra of thin crystals. These bands are also found in reflection spectra of thick samples out where is a negligible transparency. These bands appear in reflection spectra at energies 2.591 eV (***α***), 2.628 eV (***β***), 2,728 eV (***α****), 2.765 eV (***β****) and 2.864 eV (***γ***). Amplitudes of ***α*** and ***β*** bands reflectivity changing (distance between maximum and minimum of respective band) are corresponded to 2 - 2.5%. Energy splitting of bands ***α*** - ***β*** and ***α**** - ***β**** are 37 meV. The distance between ***α***(***β***) and ***α****(***β****) is equal to 167 meV. Received data have a good agreement with Refs. [6].

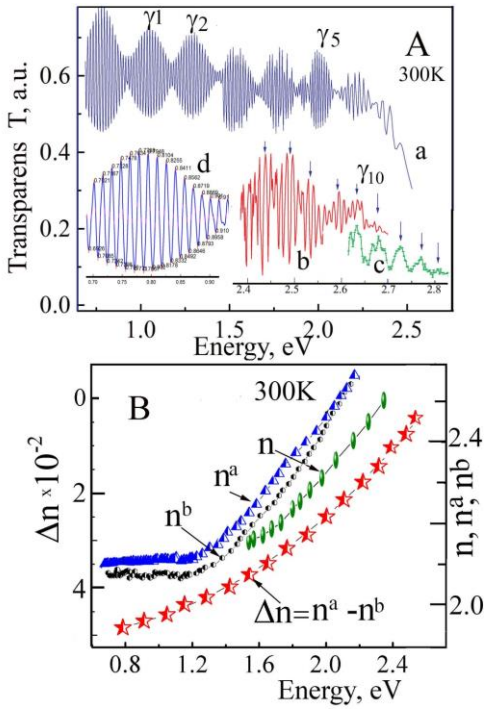

Fig. 2 A - Transmission spectra of $ZnIn_2S_4$ crystals of 47 μm (a, d), 27 μm (b) and 17 μm (c) thicknesses measured at temperature 300 K. B - Spectral dependences of refractive indices in polarization ***E*||*a*** (**n**^{a}), ***E*||*b*** (***n***^{b}) and in nonpolarized light (***n***) and refractive indices difference ***Δn = n**^{a} - **n**^{b}** measured at 300 K.

It is known from general theory of optical phenomenon in semiconductors, that direct electron transitions are observed in reflection spectra. Since the discussed transitions are found in reflection and absorption spectra out, one can assume that they are due to impurity or like Frenkel excitons states, as in the case of $PbGa_2S_4$ crystals [7]. One can supposed that bands ***α*** and ***β*** are caused by ground state (n = 1) and bands ***α**** and ***β**** due to excited state (n = 2) of Frenkel excitons. In this case, the Rydberg constant ***R*** is of the order of 220 meV, and by virtue of this, these bands are detected at room temperature. Perhaps the maxima ***α***, ***β***, ***α**** and ***β**** are all related to the ground states and reflect the complex structure of the valence bands in ***k*** = 0.

The small magnitude of reflectivity changing (2 - 2.5%) is caused by small bond between layers of $ZnIn_2S_4$ crystal structure.

Transmission spectra of crystals with different thicknesses were measured for calculation of refractive indices dependences. Figure 2, A shows transmission spectra of crystals of 47 μm (a) measured at temperature 300 K. One can see the thin structure of Fabry-Perot interference which is grouped into fringes package (marked as ***γ1***, ***γ2*** etc.). Measured experimental transmission and reflection interference spectra were work up to corresponding mathematical program which determine maxima and minima positions (see curve d in Fig. 2, A).

Figure 2, B shows spectral dependences of refractive indices ***n**^{a}* for ***E*||*a*** polarization, ***n**^{b}* fro ***E*||*b*** polarization and n for nonpolarized case. Spectral dependences of refractive indices difference (***Δn = n**^{a} - **n**^{b}***) were determined from interference fringes packets marked as ***γ1***, ***γ2*** etc. Refractive indices ***n**^{a}* and ***n**^{b}* at temperature 300 K are grown with energy increasing and they are practically equal at energy ~ 2.2 - 2.3 eV. This is also confirmed by calculated values of the refractive index difference ***Δn = n**^{a} - **n**^{b}*** whose minimum value is also in this energy range.

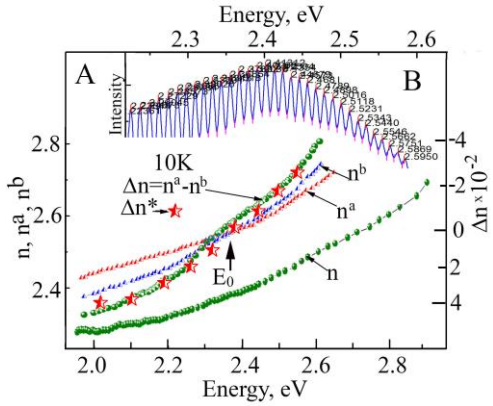

Fig. 3 Spectral dependence of refractive indices in nonpolarized light (***n***) and in ***E*||*a*** (***n**^{a}*) and ***E*||*b*** (***n**^{b}*) polarizations and refractive indices differences ***Δn****, ***Δn = n**^{a} - **n**^{b}*** for $ZnIn_2S_4$ crystals measured at 10 K. Insert shows an fragment of interference maxima determination.

Figure 3 shows spectral dependences of refractive indices in ***E*||*a*** (***n**^{a}*), ***E*||*b*** (***n**^{b}*) polarizations, in nonpolarized light (***n***) and refractive indices differences ***Δn****, ***Δn = n**^{a} - **n**^{b}*** in $ZnIn_2S_4$ crystals measured at 10 K. The inset B shows the fragment of the position of the interference maxima. Spectral dependence ***Δn**** was calculated from energy position of interference fringes revealed in interval 2 - 2.6 eV for crystals with different thicknesses (marked by asterisks in Fig. 3). The magnitude of ***Δn*** is determined as difference ***n**^{a} - **n**^{b}***. The value of ***Δn*** at 10 K is positive for energies E < 2.38 eV and negative in region E > 2.38 eV (see Fig. 3). Changing of ***Δn*** determined from Fbary-Perot interference from plane-parallel $ZnIn_2S_4$ planes and from birefringence interference is practically the same, Fig. 3.

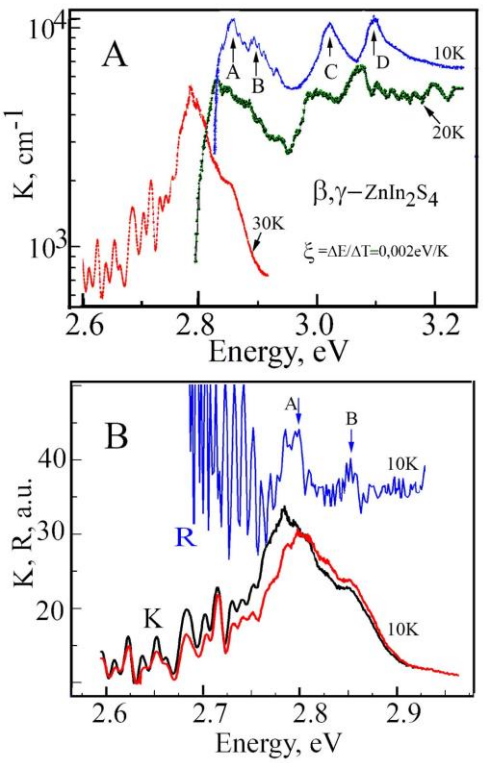

Fig. 4, Absorption (K) and reflection (R) spectra of $ZnIn_2S_4$ crystals (β and γ polytypes) with 7,5 - 12 μm thickness measured at temperatures 10, 20 and 300 K.

Maxima ***A***, ***B***, ***C*** and ***D*** at energies 2.802 eV, 2.851 eV, 3.029 eV and 3.107 eV, respectively are observed in adsorption spectra of $ZnIn_2S_4$ crystals of 11 -12 μm thickness measured at temperatures 10, 20 and 30 K (see Fig. 4). Adsorption spectra of crystals of 12 μm thickness and reflection spectrum of 7.5 μm sample measured at 10 K are presented on Fig. 4, B for comparison. Broad bands were distinguished at energies 2.802 eV and 2.851 eV in adsorption spectra and in the reflection spectrum at similar energies. The interference fringes are put over the main bands contours. A splitting of ***A*** and ***B*** bands is equal to 48 meV and it for ***C*** and ***D*** bands is 78 meV.

The maxima of reflection and absorption spectra ***α*** and ***β*** (see Fig. 1) were observed in $ZnIn_2S_4$ crystals in the band gap minimum localized in $\boldsymbol{k} = 0$ in $\boldsymbol{E} \perp \boldsymbol{c}$ polarization. These features are probably caused by transitions from Frenkel's excitons levels. Maxima ***α**** and ***β**** are due to Frenkel's excitons formed by valence bands $\boldsymbol{V_3}$ and $\boldsymbol{V_4}$ and conduction band $\boldsymbol{C_1}$. In this case for ***α*** polytype top valence bands $\boldsymbol{V_1}$ and $\boldsymbol{V_2}$ splitting is equal to 37 meV. Valence bands $\boldsymbol{V_3}$ and $\boldsymbol{V_4}$ are split on the same value. The splitting value between pairs of bands $\boldsymbol{V_1}$, $\boldsymbol{V_2}$ and $\boldsymbol{V_3}$, $\boldsymbol{V_4}$ is 161 meV. In the case of ***β***-polytype crystals the maxima in reflection and absorption spectra in energy diapason 2.6 - 2.8 eV are not observed at all. Only maxima ***A*** and ***B*** splitting on 48 meV in reflection and adsorption spectra are discovered in ***β***-polytype crystals (see Fig. 4). These features are due to direct electron transitions between pairs of bands $\boldsymbol{V_1}$, $\boldsymbol{V_2}$ and band $\boldsymbol{C_1}$. In crystals of this polytype the maxima ***C*** and ***D*** are observed at higher energies in adsorption spectra at temperature 10 K. These maxima are caused by electron transitions from bands $\boldsymbol{V_3}$, $\boldsymbol{V_4}$ to band $\boldsymbol{C_1}$. For this polytype the valence bands $\boldsymbol{V_3}$ and $\boldsymbol{V_4}$ are splitting on 78 mV and an energy distance between bands $\boldsymbol{V_2}$ and $\boldsymbol{V_3}$ are 185 meV.

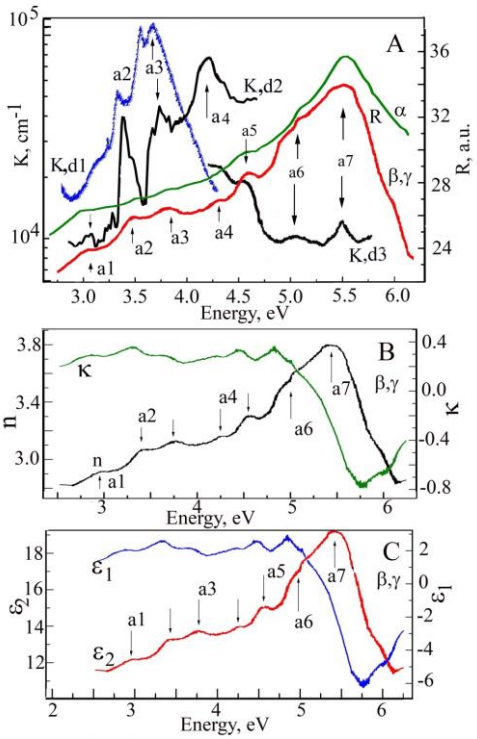

Fig. 5, A - Absorption (***K***) spectra of $ZnIn_2S_4$ nanocrystals with different thicknesses (***d1*** - 620 nm, ***d2*** - 540 nm and ***d3*** - 210 nm) and reflectin (***R***) spectra of thick crystals (1,1 mm) measured at 300 K. B, C - spectral dependences of refractive index (***n***), extinction coefficient (***κ***), real ($\boldsymbol{\varepsilon_1}$) and imaginary ($\boldsymbol{\varepsilon_2}$) parts of permittivity.

Absorption bands at energies 3.055 eV (***a1***), 3.305 eV (***a2***), 3.404 eV (***a3***), 3.759 - 3.777 eV (***a4***) were observed at higher energies of absorption spectra of $ZnIn_2S_4$ nancrystals of 620 nm (***d1***) and 540 nm (***d2***) thicknesses (see Fig. 5). Weak features in absorption spectra of thinner sample (210 nm ***d3***) were distinguished at energies 4.541 eV (***a4***), 4.774 eV (***a5***), 5.165 eV (***a6***) и 5.573 eV (***a7***). Reflection spectra in intrinsic region (2 - 6 eV) measured on thick crystal (d ~ 1.1 mm) contain reflection maxima (a1 - a7) at energies coinciding with ones from adsorption spectra (see Fig. 5). These reflection maxima discovered in intrinsic adsorption region are caused by direct electron transitions between valence and conduction bands.

Thereby a difference in band gap energy for polytypes exists but it is not essential. The interband minimum for ***α*** polytype is less than gap of ***β*** and ***γ*** polytypes. The magnitudes of bands splitting for different polytypes differ insignificantly. Maxima are found out at higher energies ($\boldsymbol{E} > 3.1$ eV) both in reflection and adsorption spectra (see Fig. 5). Figure 5 shows reflection and transmission spectra of ***β*** and ***γ*** polytypes and reflection spectra of ***α*** polytype. It was not possible to select nanocrystals for adsorption measuring at high-energy region for ***α*** polytype as it was made for crystals of ***β*** and ***γ*** polytypes.

Reflection spectra in region of fundamental electron transitions for α polytypes and β and γ polytypes have a similar contours and features. Maxima are observed at the same energies but in β and γ polytypes maxima (features) are more graphically pronounced (see Fig. 5). Using spectral dependences of measured reflectivity the spectral dependences of optical constants (n, κ, ε_1 and ε_2) were calculated by help of Kramers-Kronig relations (Fig. 5, B and C).

As mentioned above the features in absorption and reflection spectra (α, β, α^* and β^*) discovered in α polytypes and maxima (A, B, C and D) observed in β and γ polytypes are due to direct electron transitions in Brillouin zone center from V_1, V_2, V_3 and V_4 bands to conduction band C_1.

IV. Conclusions

Spectral dependences of refractive indices n^a ($E||a$) and n^b ($E||b$) of light waves and its intersection at energy E_0 ~ 2.8 eV were determined by investigation of interference spectra of $ZnIn_2S_4$ crystals of different thicknesses (7.5 - 900 μm). In energy range 08 - 3.0 eV spectral dependence of refractive indices difference $\Delta n = n^a - n^b$ was calculated. Band-to-band electron transitions in k = 0 were revealed in reflection and absorption spectra and valence bans V_1, V_2 and V_3, V_4 splitting was determined. Electron transitions in energy interval 2 - 6 eV were identified according actual theoretical band structure calculations.

References

[1] N.A. Goryunova, Compound diamond-like semiconductors, Moskow, Sov. Radio, 1968.
[2] Yang Xia, Qin Li, Kangle Lv, Mei Li, Appl. Surf. Sci. 398 (2017) 81.
[3] A. Anede, L. Cugusi, E. Grilli, M. Guzzi, F. Raga, A. Spiga, Solid State Commun. **29** (1979) 829.
[4] F. Aimerich, F. Meloni, G. Mula, Solid State Commun. 29 (1979) 235.
[5] Masood Yousaf, M. A. Saeed, Ahmad Radzi Mat Isa, H. A. Rahnamaye Aliabad, M. R. Sahar, Chin. Phys. Lett. 30(7) (2013) 077402.
[6] A.N. Georgobiani, S.I. Radautsan, N.M. Tighinyanu, Sov. Phys. Semicond**. 19** (1985) 193.
[7] I.G. Stamov, N.N. Syrbu, V.V. Ursaki, V.I. Parvan, V.V. Zalamai, Opt. Commun. 285(24) (2012) 5198.