Large Oscillator Strength Excitons in $PbGa_2S_4$ Crystals

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***Abstract* – In $PbGa_2S_4$ crystals the exciton states with the energy of about 290 meV and high oscillator strength (longitudinal – transversal dissipation of 75 meV) were observed. The ground states of the excitons are not dissociated at the room temperature. At the temperature of 77 K and 8.6 K the ground (n=1) and excited (n=2,3) states of two excitons series A and B are observed. The Bor radius for A excitons is about 70 Å and for B excitons is about 10Å.**

***Index Terms* – $PbGa_2S_4$, excitons series, Bor radius for excitons, excitons with large binding energy and oscillator strength, parameters of excitons**

I. INTRODUCTION

Usually, the excitons are not observed in semiconductors at room temperature due to low value of their exciton binding energy. The efficiency of absorption and refraction at the exciton resonance frequency is low due to the week exciton strength and the high values of the exciton radius. According to the literature data [1,2], two factors restrain the implementation of semiconductors in optoelectronic devices: (i) the low value of exciton binding energy and the dissociation of excitons at room temperature, and (ii) the low contribution of exciton states to the optical constants of crystals (the low value of the exciton oscillator strength) due to the high values of the exciton radius.

In this paper we present results of investigation of exciton states in $PbGa_2S_4$ crystals with the ground state Bohr radius of 70 Å and 10 Å. The excitons with the Bohr radius of 10 Å are observed at both low and room temperatures. Apart from that, excited n = 2 and n = 3 states are observed al low temperature. The reflectivity spectra contours are calculated and the main exciton parameters are determined. A model of bands responsible for exciton transitions at K=0 is proposed.

II. EXPERIMENTAL DETAILS

$PbGa_2S_4$ crystals are promising materials for photo-detectors sensitive in the UV region. These crystals has wide ban, with a band gap > 3 eV. Exciton transition are detected at room temperature. Reflection and transmission spectra were measured on JASCO-870 spectrometer, spectra at 10K were measured on СДЛ-1 spectrometer in cryostat LTS-22 C330 Workhorse type Optikal. The comaund $PbGa_2S_4$ crystallizes in rombic lattice with space group D_{2h}^{24} with parameters a=20.706 Å, b=20.380Å, c=12.156 Å [7, 8]. Edge absorption is due to direct allowed transition. For the polarization E||c and E⊥c the edge absorption split to 20-25 meV.Line spacing: single. Text organization: two columns. Column width: 8.3. Space between columns: 0.9 cm. Last page columns must be equal in length. Header and footer: different for odd and even pages. In the reflection spectra of $PbGa_2S_4$ crystals at the minimum of interband interval at 10K in the polarization E‖c and E⊥c were detected lines at 3,042eV ones and weaker line at 3,094eV.

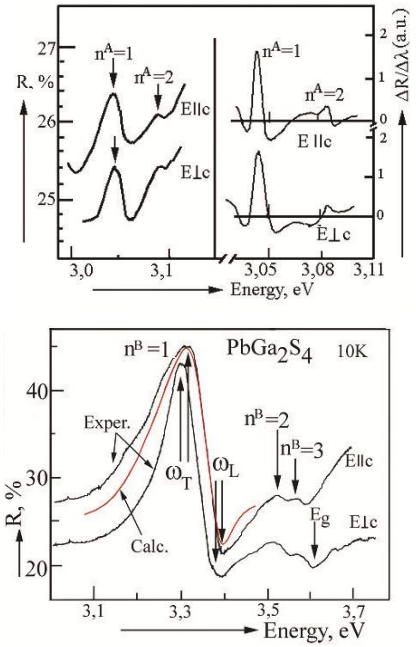

Fig.1 Reflection spectra and wavelength-modulated reflection spectra of crystal $PbGa_2S_4$ in the polarization E‖c and E⊥c measured at 10K and calculated by the dispersion relation contour of reflection spectra for polarization E‖c

The reflection spectra in the vicinity of these lines has traditionally form characteristic excitons with maximum and minimum. Maximum of reflection spectra at 3,042eV is the basic state n=1 and maximum at 3,094eV is the excited state n=2 of longwave exciton series A (series conventionally designated A). In the spectra form Fig.1 clearly stand out the minima of reflection spectra at 3,053eV. These features are due to the presence of transversal (maximum) and longitudinal (minimum) of excitons. Based on these data were estimated the energy of transverse-longitudinal splitting of the basic state of A-exciton $\Delta\omega_{LT,}$ which is equal ~11meV. In the right side of Fig.1 is presents the reflection spectra modulated by the wavelength at 10K of $PbGa_2S_4$ crystals.In the polarizations E‖c and E⊥c in a modulated reflectance spectra revealed the line n = 1 (ω_t = 3,043eV) and n = 2 (3.096eV). In the region of exciton resonance reflection coefficient is 0.24-0.25, and ε_d varies in the range 7.4-8.2. The calculations used the value of the background

dielectric constant near the exciton resonance. When ε_d = 7.6 and 7.0 reduced effective mass of the A-exciton $\mu = \varepsilon_b^2 R/R_H = 0.352 m_0$, where - R_{H_2} the energy of the Rydberg hydrogen atom (13.6 eV). Rydberg constant R, obtained from the calculations on lines n = 1 and n = 2 is equal to 0.070 eV. The minimum gap width at 10 K is 3.112 eV. In the short-wavelength region of the exciton A series of reflection spectra revealed intense peaks at an energy of 3.326 eV for polarization E‖c and at an energy of 3.317 eV for polarization E⊥c. These lines are due to the base state n = 1 exciton of B series. In the short-wave region were detected maxima at energies 3.544 eV and 3.584 eV, which are the excited states n = 2 and n = 3 in the exciton series. In the spectra clearly stand out a minimum of reflection at 3.382 eV and 3.408 eV. These minima are caused by the energy of the longitudinal exciton of B series.

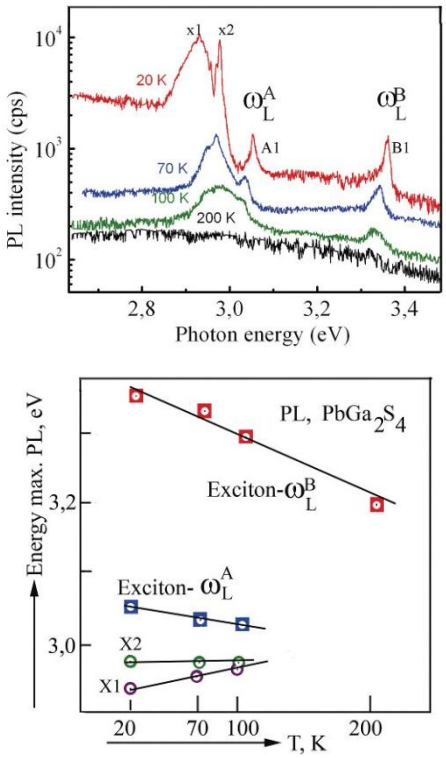

Fig.2 The luminescence spectra of $PbGa_2S_4$ crystals at temperature 20K, 70K, 100K and 200K and changes of the energy maxima of the luminescence with temperature change in the crystal.

In the photoluminescence spectra of the crystals *$PbGa_2S_4$* excited by argon laser line observed narrow emission lines x1, x2, A1 and B1 at the energies 2.9312, 2.9771, 3.0534 and 3.3613 eV, respectively. The nature of the lines x1 and x2 has the impurity character, with the temperature increases, their intensity decreases (especially peak-x2). Increase in temperature leads to a shift in luminescence peaks in energy position (Fig. 2). Temperature gradient changes of emission maxima position for ω_L^B and ω_L^A within the limits of experimental error coincide. Temperature gradient changes of the maxima energy position for x1 and x2 differ (Fig. 2), which indicates extrinsic nature of these peaks. Most likely, these peaks are due to bound excitons. The energy position of lines A1 and B1 correspond to the energy of longitudinal excitons A and B. The estimated value of the transverse-longitudinal splitting $\Delta\omega_{LT}$ (were taken the difference between the energy minimum and maximum of reflection spectra) of B-excitons for the polarizations E‖c and E⊥c is equal with 50 and 52 meV. Considering the energy position of the base and excited states of B-excitons was defined Rydberg constant which is equal with 291 meV in the polarization E‖c and 292meV in the polarization E⊥c. Taking into account magnitude of background dielectric constant (7,6-7,0) was calculated the B-exciton reduced mass μ , which is equal with 1,126 m_0. Energy of continuum for B exciton series is equal with 3.617 eV (E‖c) and 3.610 eV (E⊥c). The values obtained for the binding energy 291-292 meV for B-excitons in crystals $PbGa_2S_4$ are near a record for the crystals with a bandgap of 3 eV. Exciton energy exceeds 290 meV are observed in crystals [1]. In NaI crystals the Rydberg constant is equal with 300 meV in the KI crystal binding energy is equal with 400 meV. In other alkali-halide crystals the binding energy is more. Excitons with the same binding energy is related to the Frenkel exciton. [1].

Thus, the observed exciton states in a series of crystals $PbGa_2S_4$ can be attributed to the Frenkel exciton, and it should be noted that the crystals are $PbGa_2S_4$ narrower gap than the crystals of KI and NaI. The difference in bandgap crystals $PbGa_2S_4$ and KI (NaI) is equal to 2.3 eV.

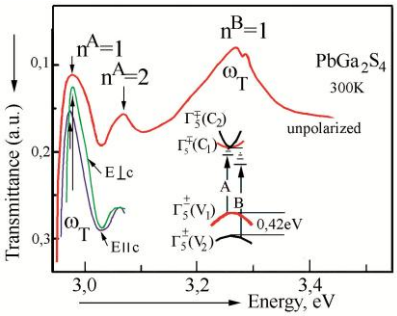

Fig.3 The transmission spectra of $PbGa_2S_4$ crystals measured at 300K in the polarizations E‖c (curve shifted vertically downwards by 0,5, E⊥c and in unpolarized light (the thickness of the crystals 17 microns).

In Figure 3 shows the transmission spectra of $PbGa_2S_4$ crystals at 300K in a polarized and not polarized light. In the transmission spectra revealed state n = 1 and n = 2 for A-excitons, respectively, at energies 2.990 eV and 3.044 eV.

TABLE 1. *PARAMETERS OF EXCITONS AND BANDS OBTAINED FROM THE CALCULATIONS OF THE OPTICAL REFLECTION SPECTRA AND WAVELENGTH-MODULATED REFLECTION SPECTRA OF $PBGA_2S_4$ CRYSTALS*

Parameters	E‖c, 10K, ε_∞ = 7.6		E⊥c, 10K, ε_∞ = 7.0	
	A	B	A	B
ω_0, eV	3.042	3.326	3.042	3.317
ω_{LT}, meV	11	50	11	52
γ, meV	0.19	60	0.16	60
t, Å	25	20	25	20
M, m_0	3	5	3	5
R, eV	0.070	0.291	0.070	0.292
μ, m_0	0.352	1.134	0.352	1.134
m_C^*, m_0	0.17	1.71	0.17	1.71
m_V^*, m_0	2.83	3.29	2.83	3.29

The difference in energy for base state n = 1 in the polarization E‖c and E⊥c does not exceed 20 meV. At the energy of 3.257 eV observed maximum of absorption due to

transitions to the base state of transversal B-excitons. Taking into account the energy position of n = 1 and n = 2, Rydberg constant is equal to 90 meV. This value coincides with the binding energy determined at 10K. Using the conditions $M = m_V^* + m_C^*$ and $\frac{1}{\mu} = \frac{1}{m_V^*} + \frac{1}{m_C^*}$ were calculated the effective mass of electrons and holes which are responsible for A and B series of excitons (Table 1).

As seen from the table, the effective mass of electrons and holes are responsible for A and B exciton series are different. These data indicate that the exciton series A is formed by a pair of zones $V_1 – C_1$ and Series B is formed by a pair of zones $V_2 – C_2$. Effective Bohr radius a_{ex} are defined by formulas of Bohr for hydrogen atom

$$a_{ex} = a_B \varepsilon m_0 / \mu$$

where a_B the Bohr radius of hydrogen atom, ε and μ-dielectric constant and the reduced effective exciton mass. In discussed crystal $PbGa_2S_4$ exciton base state (n = 1) have different radii of Bohr. For A-excitons a_B is 70 Å, and for B-excitons in aB is 10 Å. Thus, we see two different exciton with different Bohr radius. A series of excitons refer to Wannier-Mott excitons and B series can be considered the Frenkel exciton. Exciton parameters are given in Table 1.

We will analyze the energy band structure of PbGa2S4 crystals taking into account the exciton transitions discussed above. The wave functions of the valence and conduction bans of PbGa2S4 crystals are transformed according to the irreducible representations Γ_5^+ or Γ_5^- of the point symmetry group D_{2h} [23]. Therefore, one needs to consider the selection rules of transitions from the ground crystal state |0> to the exciton K, Γex, j> state, i. e. the conditions of difference from zero of the matrix element of the transition <0|Hint|K, Γex, j>, where K is the exciton wave vector, Γex is the irreducible representation according to which the wave function of the exciton is transformed, j is the row, Γex is the direct product of the irreducible representations $\Gamma_l \times \Gamma_h \times D_l$ (i = 0,1…) according to which the wave functions of electrons, holes and their relative motion are transformed. The transitions occur under the action of the light. In the $PbGa_2S_4$ crystals Γ_2^- excitons are dipole-active in the E||b, (k||a, k||c) polarization, while the Γ_3^- excitons are active in the E||c, (k||a, k||b) polarization, and the Γ_4^- excitons are dipole-active in the E||a, (k|b, k|c) polarization.If one compares the obtained experimental results with the exciton symmetries, one can note that the long-wavelength A-excitons with Γ_3^- and Γ_4^- (or Γ_2^-) symmetry have similar parameters. The splitting of the ground exciton states does not exceed 20 meV. The symmetry of the B-excitons is the same as that of A-excitons. The energy position of the n = 1 state of B-excitons in the E||c and E⊥c polarizations also does not exceed 20 meV. On the basis of the selection rules and the obtained values of electron and hole effective masses, one can propose a following model of energy bands explaining the exciton spectra: the A-exciton series is formed by the (V1-C1) bands with $\Gamma_5^{\pm} - \Gamma_5^{\mp}$ symmetry, while the B-exciton series is produced by the V2-C2) bands with $\Gamma_5^{\pm} - \Gamma_5^{\mp}$ symmetry. According to this model, the both exciton series are produced in the center of the Brillouin zone as shown in Fig. 7. The C1 and C2 bands are probably degenerated in the center of the Brillouin zone, since the bandgaps for the E⊥c and E||c polarizations obtained from exciton spectra coincide in the limits of experimental errors.

III. CONCLUSION

In conclusion, we note that the crystals were first discovered $PbGa_2S_4$ excitons with large binding energy and oscillator strength. These excitons contribute significantly to the optical constants even at room temperature. On the basis of such materials, you can create optoelectronic devices operating at room temperature, which action is based on physical principles of light interaction with excitons [2,3].

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