ELECTRICAL AND OPTICAL PROPERTIES OF $AgGaGe_2S_2Se_4$ SINGLE CRYSTALS

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Single crystals of the solid solution 50 mol.% $AgGaGeS_4$ + 50 mol.% $AgGaGe_3Se_8$ are studied. Due to a statistical distribution of Ga and Ge atoms over the relevant crystal lattice sites and the presence of vacancies at Ag sites, the solid solution exhibits properties of disordered semiconductors with the maximum density of localized energy states near the middle of the energy gap. The optical and thermal bandgap energies, as well as their temperature dependences, have been determined ($E_g \approx 2.30$ eV at $T \approx 300$ K). $AgGaGe_2Se_4$ single crystals are found to be photosensitive p-type semiconductors with the Fermi level locating near the middle of the bandgap. The peculiarities in the conductivity of the samples and the spectral distribution of their photoconductivity have been examined. A consistent physical model that explains the experimental results has been suggested.

1. Introduction

At present, the single crystals of ternary compounds $AgGaS_2$ and $AgGaSe_2$ are ones of the most widespread substances used for the parametric generation of light in the middle-infrared range. The largest scope of application of the parametric crystals includes powerful CO and CO_2 lasers. Tetradic compounds $AgGaGeS_4$ and $AgGaGe_3Se_8$ are analogs of $AgGaS_2$ and $AgGaSe_2$, respectively. They were discovered, while attempting to improve the parameters of ternary phases by adding germanium dichalcogenides. Besides that their resistance to the action of laser irradiation is twice as high, the magnitude of birefringence in tetradic compounds is larger, the transparency region increases, and the melting temperature diminishes, which is favorable for the technology aimed at fabricating the good-quality crystals. $AgGaGeS_4$ and $AgGaGe_3Se_8$ compounds are isostructural, and they form a continuous series of solid solutions [1].

The $AgGaGe_2S_2Se_4$ phase is a part of this series with a content of 50 mol.% $AgGaGe_3Se_8$. To grow the corresponding crystals, we used the Bridgman–Stockbarger technique. The growth zone temperature in a two-zone furnace was 1170 K, and that of the annealing zone was 750 K, so that a temperature gradient of 3 K/mm was created at the crystallization front. The crystal was annealed for 200 h. Afterwards, it was cooled down to room temperature at a rate of 5 K/h. Single crystals fabricated in such a manner were light-red colored. Their average dimensions were 35 mm in length and 9 mm in diameter.

X-ray diffraction researches showed that the crystals of the $AgGaGe_2S_2Se_4$ phase belong to spatial group $Fdd2$, with lattice parameters $a = 1.22746(5)$ nm, $b = 2.3541(1)$ nm, and $c = 0.70539$ nm. In this structure, sulfur and selenium atoms occupy three sixteen-fold positions $16b$ in the 1:1 ratio. The same position is occupied by Ag atoms with a probability of 56.3%. Ga and Ge atoms statistically occupied two crystallographic positions, $8a$ and $16b$, with probabilities of 37.5 and 62.5%, respectively. The statistical distribution of Ga and Ge atoms over the crystal lattice of the $AgGaGe_2S_2Se_4$ solid solution brings about a random fluctuation of the electric potential and makes the solution closer to a disordered state [2].

2. Experimental Results and Their Discussion

In this work, we studied some electrical, optical, and photo-electrical properties of $AgGaGe_2S_2Se_4$ single crystals grown by us. These single crystals are high-resistance substances with the dark electric conductivity $\sigma \approx 2 \times 10^{-8}\ \Omega^{-1}\mathrm{cm}^{-1}$ at room temperature $T \approx 293$ K. Low values of thermal e.m.f. coefficient ($\alpha \approx 10 \div 20\ \mu$V/K) and σ testify to a deep position of the Fermi level E_F (namely, near the middle of the energy gap) in solutions with close contributions of electron and hole components to α [3]:

$$\alpha = \frac{\alpha_p \mu_p p - \alpha_n \mu_n n}{\mu_p p + \mu_n n}, \qquad (1)$$

where μ_p and μ_n are the mobilities of holes and electrons, respectively, in the bands; p and n are, respectively, the hole and electron concentrations; and α_p and

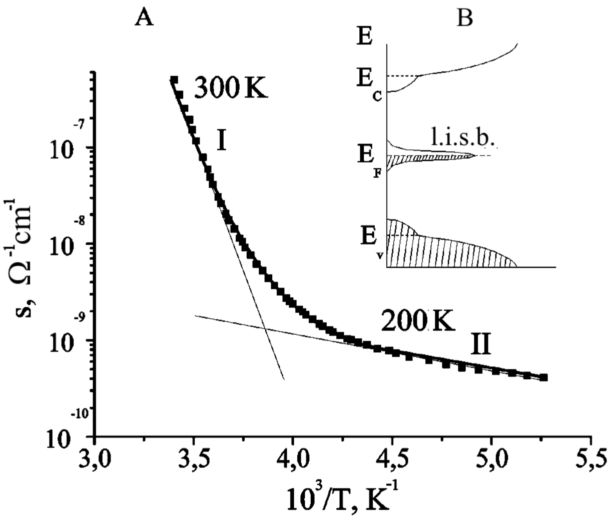

Fig. 1. (*A*) Temperature dependence of the electric conductivity in $\mathrm{AgGaGe_2S_2Se_4}$ single crystals; (*B*) the distribution of electron defect states in a disordered semiconductor (the Davies–Mott model). E_c and E_ν are boundary energies that separate localized and non-local states; l.i.s.b. – localized-impurity-state band

α_n are the corresponding partial thermal e.m.f. coefficients. For the majority of semiconductor materials, $\mu_p < \mu_n$. Therefore, the small positive value of α testifies to the conductivity of the p-type in $\mathrm{AgGaGe_2S_2Se_4}$, which may be associated with a certain excess of the hole concentration in comparison with the electron one.

In Fig. 1, the temperature dependence of the dark electroconductivity, $\sigma(T)$, for $\mathrm{AgGaGe_2S_2Se_4}$ single crystals is shown. As is seen from the figure, in the temperature intervals denoted as I and II, the function $\sigma(T)$ can be presented as the exponential dependence

$$\sigma = \sigma_0 \exp\left(-\frac{E_A}{kT}\right), \tag{2}$$

which is typical of the disordered semiconductors [4]. The activation energy E_A for the electric conductivity in region I ($T > 270$ K) determined from Eq. (2) is equal to $E_{A\mathrm{I}} \approx (1.14 \pm 0.03)$ eV.

In defect crystals, owing to the random distribution of the potential of the electric field induced by a static distribution of Ga and Ge atoms over sites of the crystal lattice of a solution and by fluctuations in the concentration of charged structural defects, there emerge tails in the density of electron states, which adjoin the edges of allowed energy bands and create the bands of localized defect states in the forbidden gap. The density of states in those bands is so high that the Fermi level becomes pinned [4] (Fig. 1). The magnitude of preexponential factor σ_0 in Eq. (2) turned out to be equal to $\sigma_{01} \approx (5 \times 10^2 \div 1 \times 10^3)\ \Omega^{-1}\mathrm{cm}^{-1}$ at $T \geq 270$ K for various crystals. According to the model of electron states in disordered systems [4], this fact testifies to the thermally induced excitation of holes from the levels close to E_F into non-localized states in the valence band. Adopting that the Fermi level lies near the middle of the energy gap (Fig. 1,*B*) – as was marked above, this suggestion follows from the low α-value and the low conductivity of specimens (compensated) – the thermal width of the energy gap can be estimated to equal $E_{gT} \approx 2E_{A\mathrm{I}} = (2.28 \pm 0.03)$ eV.

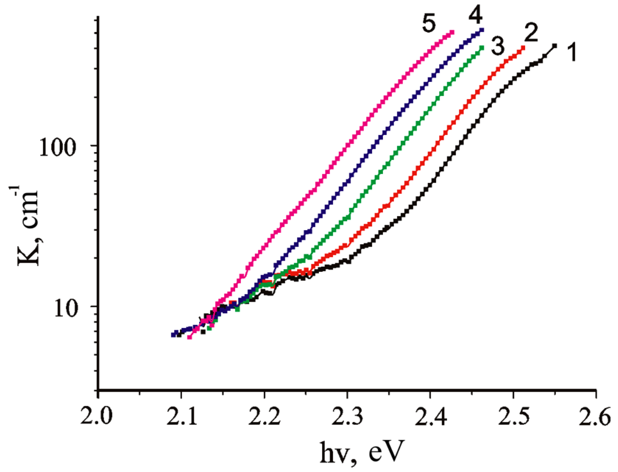

Fig. 2. Spectra of the optical absorption of light in $\mathrm{AgGaGe_2S_2Se_4}$ single crystals at temperatures of 100 (*1*), 150 (*2*), 200 (*3*), 250 (*4*), and 300 K (*5*)

In low-temperature section II ($T < 200$ K), the activation energy of electric conductivity equals $E_{A\mathrm{II}} \approx (0.07 \pm 0.03)$ eV, and the preexponential factor $\sigma_{0\mathrm{II}} \ll \sigma_{0\mathrm{I}}$. This behavior of $\sigma(T)$ is typical of the hopping mechanism of conductivity between the nearest neighbors through the impurity-defect band, which makes E_F fixed. The hopping activation energy, $E_{A\mathrm{II}}$, is close to half the bandwidth of the localized defect state band [4].

An important information on the defect state of a semiconductor is given by researches of the frequency dependence of the absorption coefficient, $K(\nu)$, at the fundamental absorption edge (FAE). As is seen from Fig. 2, the dependence $K(\nu)$ in the FAE region is described well by an exponential dependence, which is often referred to as the Urbach rule [2],

$$K(\nu) \sim \exp\left(-\frac{E_g - h\nu}{\Delta_0}\right). \tag{3}$$

If dependence (3) is obeyed, this means that the optical transitions in the FAE region are formed with the participation of tails of the density of states (their emergence

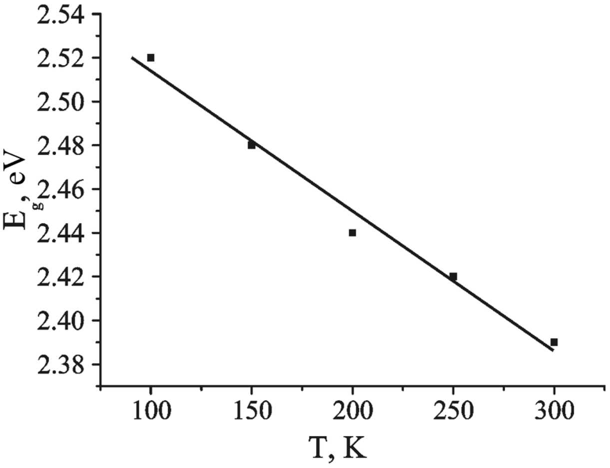

Fig. 3. Temperature-induced variation of the energy gap width in $AgGaGe_2S_2Se_4$ single crystals

is associated with the crystal imperfection) adjacent to the edges of allowed bands [2].

The characteristic energy, which is responsible for the degree of crystal lattice disordering, when being calculated from the exponential dependence (3), is equal to about 0.07 eV (as it takes place in amorphous semiconductors [5]) and does not change within the temperature interval 77–300 K. Accordingly, the FAE undergoes a parallel displacement if the specimen temperature varies (Fig. 2). A large value of Δ_0 and its temperature independence evidence a considerable presence of defects in $AgGaGe_2S_2Se_4$ single crystals, namely, static structural defects of a technological origin. Assuming the impurity centers to be single-charged and using the experimentally determined value of Δ_0, we applied theoretical formulas presented in work [2] – e.g., $\Delta_0 = 2,2(n_t a_B^3)^{2/5} E_B$ – to evaluate the concentration of single-charged point defects that are responsible for the smearing of the fundamental absorption band. The corresponding obtained value equaled $n_t \approx (1 \div 2) \times 10^{18}$. While calculating n_t, we took the effective mass of an electron in the conduction band to equal $m_c \approx 0.2 m_0$ (m_0 is the free electron mass), which is valid for many binary chalcogenide semiconductors.

$AgGaGe_2S_2Se_4$ solid solutions belong to single crystals with a deficiency of Ag atoms at the crystal lattice sites in position 16*b*, which was mentioned above. As a result, the solutions contain stoichiometric vacancies of silver, V_{Ag}, the concentration of which, in accordance with the results of X-ray diffraction studies, amounts to $N \approx 10^{20}$ cm^{-3}. Cation vacancies in chalcogenide compounds play the role of acceptors. For a lot of binary chalcogenides of group $\mathrm{A^{II}B^{VI}}$ – in particular, these are solid solutions CdS–CdSe, which are analogs of the solutions under consideration – the energies of cation vacancies are close to the middle-gap energy [6, 7]. If it is true for single crystals of $AgGaGe_2S_2Se_4$ solutions, the most probable hypothesis is that the band of localized states near the middle of the energy gap in the solution, which pins E_{F}, is coupled with V_{Ag}. The acceptor character of V_{Ag} may probably be responsible for the *p*-conductivity in $AgGaGe_2S_2Se_4$ single crystals and the FAE smearing.

As was indicated above, the magnitude $\Delta_0 \approx 0.07$ eV is determined by the concentration of single-charged defects, $n_t \approx 10^{18}$ cm^{-3}, which is lower than the concentration of stoichiometric vacancies V_{Ag} (about 10^{20} cm^{-3}) in the solution.

Evidently, not all stoichiometric Ag vacancies play the role of single-charged acceptors V_{Ag}^-. Some of them, by interacting with various structural defects, which complex semiconductor compounds are rich in, form neutral complexes, which do not affect the random distribution of the electric field potential stemming from concentration fluctuations of charged defects. As an example of such neutral complexes, donor–acceptor pairs can serve, in which the acceptor is an Ag vacancy, and the role of donor is played by a shallow ionized defect, $(V_{\mathrm{Ag}}^- – D^+)^0$, or a V_{Ag} -aggregate. Such defects can act as centers of quick recombination, by reducing the photosensitivity of a substance, as well as centers of light absorption and dispersion, which increases the absorption coefficient in the range of transparency windows for light, the latter being equal to $K \approx 5 \div 7$ cm^{-1} in the solutions concerned. Similar phenomena were observed in other chalcogenide compounds as well [8, 9].

The optical width of the energy gap evaluated from the energy of quanta $h\nu$ (for $K = 350$ cm^{-1}) at the FAE turned out to equal $E_{g0} \approx 2.52$ eV at the temperature $T = 77$ K and $E_{g0} \approx 2.39$ eV at $T = 300$ K, which agrees with the thermal width $E_{gT} \approx 2.28$ eV ($T = 300$ K) determined above from the dependence $\sigma(T)$.

In Fig. 3, the temperature-induced variations of the optical width of the energy gap are exhibited. The calculated value for the thermal coefficient of E_g-variation,

$$\beta = \frac{E_{g77} - E_{g300}}{300 - 77}, \qquad (4)$$

amounts to 5.8×10^{-4} eV/K, the magnitude being typical of the majority of semiconductors. The temperature dependence of the energy gap width in solid solutions has a linear character in the interval from 77 to 300 K (Fig. 3),

$$E_{g0} = E_{g77} - \beta(T - 77\ \mathrm{K}).$$

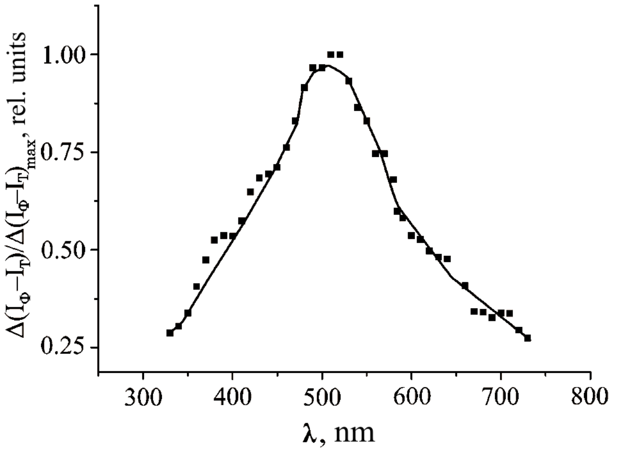

Fig. 4. Photoconductivity of $AgGaGe_2S_2Se_4$ single crystals at $T = 300$ K

In Fig. 4, the spectral distribution of the photoconductivity in $AgGaGe_2S_2Se_4$ single crystals is depicted. Here, I_T and I_Φ are the current values measured in dark and in light, respectively. A wide photoconductivity maximum observed in the FAE range evidently corresponds to the intrinsic photoconductivity. The energy gap width in the solid solution at $T = 300$ K evaluated from the photoconductivity maximum located at $\lambda_m \approx 0.563$ nm agrees well with the optical, $E_{g0} = 2.39$ eV, and thermal, $E_{gt} = 2.28$ eV, widths obtained at the same temperature. In its maximum, the electric conductivity changed by a factor of about two at an illumination intensity of 100 lx. The low photosensitivity of $AgGaGe_2S_2Se_4$ single crystals in comparison with their binary analogs may probably be associated with the presence of a high concentration of quick recombination centers connected, as a rule, with structural defects in the crystal lattice, which is confirmed by the large halfwidth (about 230 nm) of the intrinsic photoconductivity peak (Fig. 4)

3. Conclusions

Hence, $AgGaGe_2S_2Se_4$ solid solutions belong to defect semiconductors with a distribution of electron energy states $N(E)$ that confirms well the Davies–Mott model with a narrow ($\Delta \approx 0.1$ eV) maximum of localized states near the middle of the energy gap (Fig. 1,*b*). The energy gap width in the examined solid solution has been determined.

According to the high thermal stability and the electroconductivity activation energy, $E = 1.14$ eV, $AgGaGe_2S_2Se_4$ crystals are a promising material for various temperature-sensitive elements and thermistors intended for functioning at temperatures close to the room one. Being photosensitive and radiation-resistant, $AgGaGe_2S_2Se_4$ crystals can find applications in electronic and optoelectronic devices that are used in media with elevated nuclear radiation levels.

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ЕЛЕКТРИЧНІ І ОПТИЧНІ ВЛАСТИВОСТІ МОНОКРИСТАЛІВ $AgGaGe_2S_2Se_4$

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Резюме

Досліджено монокристали твердих розчинів 50 мол.% $AgGaGeS_4$ + 50 мол.% $AgGaGe_3Se_8$. Внаслідок статистичного розміщення у вузлах кристалічної ґратки атомів Ga і Ge, а також наявності вузлів не заповнених атомами Ag, тверді розчини проявляють властивості невпорядкованих напівпровідників з максимальною густиною локалізованих енергетичних станів біля середини забороненої зони. Встановлено оптичну і термічну ширину забороненої зони та їх температурну залежність ($E_g \approx 2,30$ еВ при $T \approx 300$ K). Монокристали розчину $\mathrm{AgGaGe_2Se_4}$ виявилися фоточутливими напівпровідниками p-типу провідності з положенням рівня Фермі біля середини забороненої зони. Досліджено особливості електропровідності і спектрального розподілу фотопровідності зразків розчину. Запропоновано несуперечливу фізичну модель, яка дозволяє пояснити експериментально одержані результати.