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INFLUENCE OF Cu-, Sn-, AND In-DOPING ON OPTICAL PROPERTIES OF $AgGaGe_3Se_8$ SINGLE CRYSTALS

The optical properties of $AgGaGe_3Se_8$ single crystals doped with Cu, In, and Sn atoms have been studied. A physical model is proposed for those compounds, which are wide-gap semiconductors ($E_g \approx 2.09$–2.15 eV at $T = 300$ K) with the p-type conductivity, and whose optical parameters depend on the dopant nature and concentration. On the basis of this model and making allowance for specific features of disordered systems, the obtained experimental results are explained.

Keywords: chalcogenide crystals, optical properties, Urbach energy.

1. Introduction

Progress in electronics needs the creation of new compounds with efficient and controllable properties. Anisotropic photosensitive compounds with a wide transparency window can be promising materials for their application in optoelectronics and nonlinear optics. Researches have shown that this class of materials includes multicomponent chalcogenide compounds, which are analogs of binary chalcogenides belonging to the $A^{II}B^{VI}$ group. One of those materials is the ternary chalcogenide $AgGaGe_3Se_8$ [1]. The growing technology for undoped $Ag_xGa_xGe_{1-x}Se_2$ single crystals and some of their electric and optical properties (the composition $AgGaGe_3Se_8$ corresponds to the maximum melting temperature of this phase, which possesses a wide homogeneity range) were described in works [1–3].

An important aspect of this scientific research is the expansion of the possible scope of applications, where single crystals of the $AgGaGe_3Se_8$ compound can be used. This especially concerns those of their properties that are promising for electronics, optoelectronics, and nonlinear optics: photoconductivity, luminescence, light absorption, etc. In work [4], the influence of the doping of $AgGaGe_3Se_8$ single crystals with atoms of chemical elements belonging to groups I, III, and IV on some of their optical, electric, and photo-electric properties was studied. The doped crystals were found to be disordered semiconductors with technological structural defects of the donor and acceptor types. In work [5], a laser-induced anisotropy of optical constants was revealed in a crystal of solid solution $Ag_{0.95}Cu_{0.05}GaGe_3Se_8$ (95 mol.% $AgGaGe_3Se_8$ + 5 mol.% $CuGaGe_3Se_8$) irradiated by a 150-mW continuous laser with wavelengths of 532 and 1030 nm. Hence, the insertion of impurities into the $AgGaGe_3Se_8$ crystal allows its properties to be purposefully modified.

At the same time, the study of the light absorption in crystals is a powerful method to analyze their defect states. This work is aimed at the experimental research of the light absorption in $AgGaGe_3Se_8$ single crystals doped with Cu, Sn, and In atoms. The specific task consisted in the study of the dependences of the optical absorption coefficient, the Urbach energy, and the constant of electron-phonon coupling on the temperature and the component content in the crystals concerned.

2. Experimental Methods and Equipment

Single crystals of the fourfold compound $AgGaGe_3Se_8$ were grown using the Bridgman–Stockbarger method at the technological laboratories of the Faculty of Chemistry of the Lesya Ukrainka Eastern European National University. The specimens were doped in the course of their growing. The quality of obtained single crystals was tested by means of the X-ray diffraction analysis. All calculations were carried out with

Table 1. **Concentrations of doping impurities (DIs) in $AgGaGe_3Se_8$ crystal**

Formula	Content	DI	DI concentration, at.%
$Ag_{0.95}Cu_{0.05}GaGe_3Se_8$	95 mol.% $AgGaGe_3Se_8$–5 mol.% $CuGaGe_3Se_8$	Cu	0.39
$AgGa_{0.95}In_{0.05}Ge_3Se_8$	95 mol.% $AgGaGe_3Se_8$–5 mol.% $AgInGe_3Se_8$	In	0.39
$AgGaGe_{2.85}Sn_{0.15}Se_8$	95 mol.% $AgGaGe_3Se_8$–5 mol.% $AgGaSn_3Se_8$	Sn	1.17

the help of the CSD program complex. The specimen parameters were experimentally measured, by using well-approbated standard procedures and making use of computer programs for the analysis of experimental results in the regime of their automatic registration by a recorder. A monochromator MDR-208 played the role of optical device. As a sensor of optical signals, we used a silicon-based photodetector. The temperature was measured in a liquid-nitrogen cryostat with the help of a temperature regulator Utrecs K41-3 to an accuracy of ±0.1 K. Light absorption spectra in the interval of intrinsic optical transitions were studied, by using thin specimens 0.08–0.10 mm in thickness with optically smooth plane-parallel surfaces.

3. Results of Experimental and Theoretical Researches and Their Substantiation

The phase $Ag_xGa_xGe_{1-x}Se_2$ is an intermediate fourfold compound in the system $AgGaSe_2$–$GeSe_2$ [1, 3]. Its crystalline state is characterized by the noncentrosymmetric space group $Fdd2$. Selenium atoms occupy three crystallographic positions 16*b* in the compound structure. Ga and Ge atoms are statistically distributed at positions 8*a* and 16*b*. Ag atoms occupy position 16*b*, whose filling degree diminishes if the content of germanium diselenide increases. The reduction in the concentration of silver atoms due to their removal from the $AgSe_4$ tetrahedra and the substitution of some gallium ions by germanium ones diminish the crystal lattice period. As a result, the $Se(Ga,Ge)_4$ tetrahedra become deformed, and the coordination of selenium atoms changes [6].

In this work, the optical properties of $AgGaGe_3Se_8$ crystals doped with Cu, In, and Sn atoms are studied (see Table 1). A specific feature in the structure of analyzed single crystals consists in the statistical distribution of cations (Ag, Cu), (Ga, In), and (Ge, Sn) over the crystal lattice sites and the presence of non-stoichiometric vacancies of Ag atoms (V_{Ag}) in the $AgGaGe_3Se_8$ compound [7]. A high concentration of stoichiometric silver vacancies and the statistical character of atomic distribution over the free sites of the cation sublattice are among the factors that break the long-range order in the arrangement of atoms in the crystal and the periodic character of electric potential [8, 9]. As a result, there emerge defect energy states and bands, in particular, tails in the density of states, which adjoin the band edges. Other defects can make an additional contribution to the long-range order break. All those factors make the examined phases more similar to disordered systems.

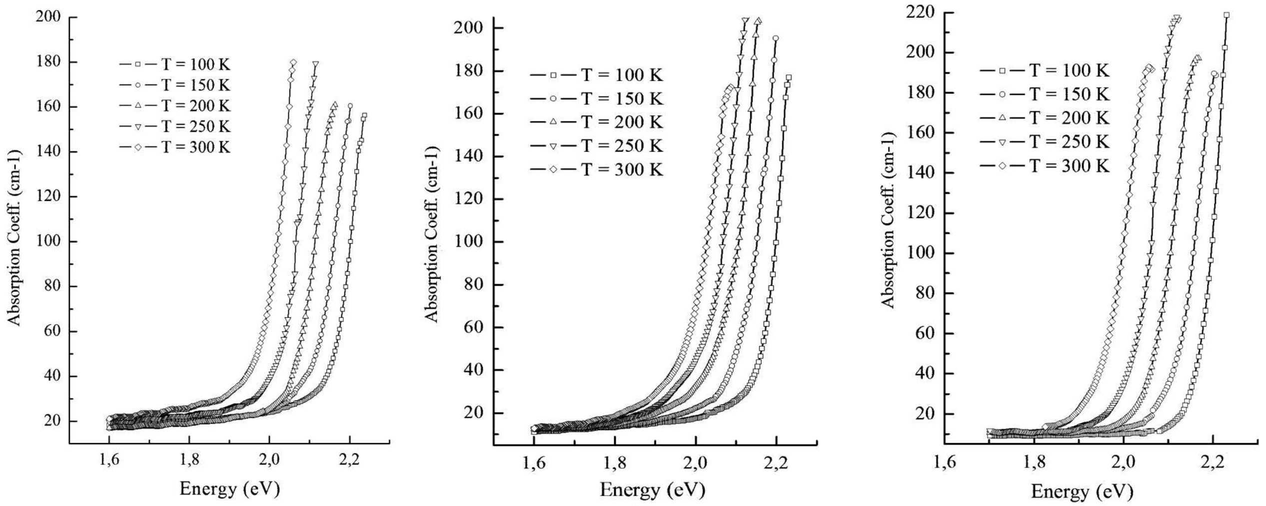
Their classification as semiconductors that reveal the features of disordered systems is confirmed by the frequency dependence of the light absorption coefficient at the edge of intrinsic optical transitions (Fig. 1). The absorption coefficient α is calculated from the relation [10]

$$T = \frac{(1-R)^2 e^{-\alpha d}}{1 - R^2 e^{-2\alpha d}},$$

where $T = I/I_0$ is the transmission coefficient, d the specimen thickness, and R the reflection coefficient. The optical absorption coefficients for various compounds were calculated, by using the R-values measured at room temperature and assuming that the temperature change from 10 to 320 K affects them only slightly [10]. The results of corresponding calculations are shown in Fig. 1.

The results obtained for the energy gap width E_g in examined crystals are quoted in Table 2. This parameter was evaluated on the basis of the energy of light quantum in the absorption edge region and putting $\alpha = 160\ \text{cm}^{-1}$. As one can see, the value of E_g depends on the temperature and the kind of doping impurity.

In our opinion, the reduction of the energy gap width is associated with the difference between the ionic radii of the elements in the compound and the substituting ion: $Cu^+(0.098\ \text{Å}) \rightarrow$



a *b* *c*

Fig. 1. Spectral distribution of the absorption coefficient for single crystals of solid solutions $Ag_{0.95}Cu_{0.05}GaGe_3Se_8$ (*a*), $AgGa_{0.95}In_{0.05}Ge_3Se_8$ (*b*), and $AgGaGe_{2.85}Sn_{0.15}Se_8$ (*c*)

Table 2. **Energy gap width evaluated at $\alpha = 160$ cm^{-1}**

Temperature, K	E_g, eV		
	$Ag_{0.95}Cu_{0.05}GaGe_3Se_8$	$AgGa_{0.95}In_{0.05}Ge_3Se_8$	$AgGaGe_{2.85}Sn_{0.15}Se_8$
100	2.34	2.31	2.29
150	2.30	2.27	2.24
200	2.24	2.22	2.21
250	2.21	2.18	2.16
300	2.16	2.14	2.10

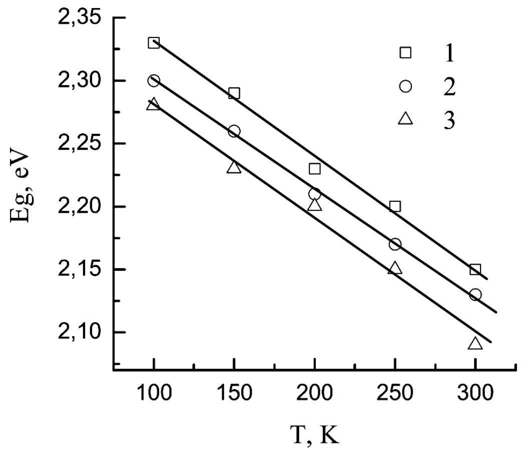
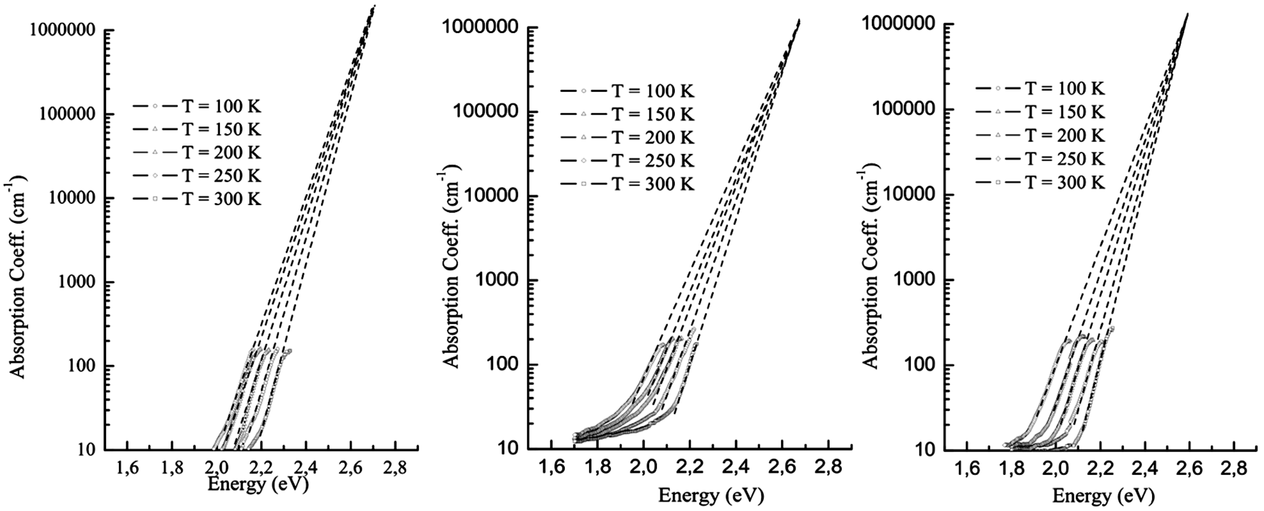


Fig. 2. Variation of the energy gap width with the temperature in single crystals of solid solutions $Ag_{0.95}Cu_{0.05}GaGe_3Se$ (*1*), $AgGa_{0.95}In_{0.05}Ge_3Se_8$ (*2*), and $AgGaGe_{2.85}Sn_{0.15}Se_8$ (*3*)

$\to Ag^+$(0.113 Å), In^{+3}(0.092 Å) $\to Ga^{+3}$(0.062 Å), and Sn^{+4}(0.067 Å) $\to Ge^{+4}$(0.044 Å) [11]. Point defects of the vacancy and interstitial types can also make an additional contribution to the change of the energy gap width. Vacancies in the crystal lattice create a deformation potential that corresponds to the lattice stretching [12]. The majority of experimental results obtained by various authors testify that the increase of the crystal lattice parameters leads to a reduction of E_g [13]. This phenomenon manifests itself well in experiments on the hydrostatic compression of crystals [12]; namely, the bulk hydrostatic pressure results in a reduction of both the interatomic distance and the energy gap width.

Our optical researches showed that the energy gap width changes almost linearly with the temperature in a temperature interval of 100–300 K (Fig. 2, Ta-



a *b* *c*

Fig. 3. Spectral distribution of the absorption coefficient in single crystals of solid solutions $Ag_{0.95}Cu_{0.05}GaGe_3Se_8$ (*a*), $AgGa_{0.95}In_{0.05}Ge_3Se_8$ (*b*), and $AgGaGe_{2.85}Sn_{0.15}Se_8$ (*c*)

ble 2). The calculated temperature coefficient for the energy gap width variation, dE_g/dT, amounts to $-(8.5 \div 9.5) \times 10^{-4}$ eV/K. All calculated temperature coefficients were negative, which allowed us to assume that the contribution of the electron-photon coupling with the growing temperature is larger than that associated with the lattice thermal expansion.

As one can see from Fig. 3, the edge of the light absorption band in all crystals is described well by the exponential dependence. To explain this fact, the assumption was put forward in work [14] that the absorption edge reflects the appearance of the tails of states owing to the fluctuations of bond angles and lengths. The other authors [15] considered that the appearance of tails is associated with electron transitions between the localized states in the tails of band edges. In its exponential section, the dependence obeys the Urbach rule [16] $\alpha = \alpha_0 \exp\left[(E - E_0)/E_{\rm U}\right]$, where $E_{\rm U} = k_{\rm B}T/\sigma(T)$ is the Urbach energy, $k_{\rm B}$ the Boltzmann constant, $\sigma(T)$ the steepness of the absorption edge, and α_0 and E_0 are the coordinates of the convergence point $\ln\alpha = f(h\nu, T)$. The approximation of absorption spectra by the Urbach formula allowed us to obtain the values for $E_{\rm U}$, α_0, and E_0, which are quoted in Table 3.

The $E_{\rm U}$-value was experimentally found to grow, when the crystal temperature increased from 100 to 300 K (Table 3). In our opinion, this fact is associated with the concentration growth of charged defects that were neutral at low temperatures, as a result of their thermal ionization.

The shape of the absorption edge is described by the empirical Urbach rule, which is satisfied for a lot of crystalline and amorphous compounds. For crystalline semiconductors at low temperatures $T < T_0$, where T_0 is a characteristic temperature, the value of $E_{\rm U}$ does not depend on T, but it does depend on the defect concentration. At $T > T_0$, the value of $E_{\rm U}$ depends on the temperature according to the law $E_{\rm U} = cT$, where c is a certain constant.

For amorphous semiconductors, T_0 is much higher than for crystalline substances, for which the Urbach rule is satisfied. For the majority of them, T_0 is located above the softening temperature. Therefore, we may consider that, for those semiconductors, $E_{\rm U}$ does not depend on the temperature.

The function $E_{\rm U}(T, x)$ is a measure of the dynamic (thermal phonons) and statistical ("frozen" phonons) disordering in the crystal lattice [15, 17]:

$$E_{\rm U}(T, x) = K(\langle U^2\rangle_x + \langle U^2\rangle_T),$$

where x is a geometrical parameter of the material, which is used to characterize the statistical disorder; $\langle U^2\rangle_x$ and $\langle U^2\rangle_T$ are the mean-square displacements of atoms in the lattice from their equilibrium positions, which are a result of the dynamical and statistical disorderings, respectively; and the coefficient K has sense of the second-order

Table 3. **Urbach rule parameters for doped $AgGaGe_3Se_8$ crystals**

Specimen	T, K	E_U, meV	n_t, 10^{17} cm^{-1}	E_0, eV for $\alpha_0 \sim 10^6$ cm^{-1}	$h\nu_0$, meV	σ_0	g
$Ag_{0.95}Cu_{0.05}GaGe_3Se_8$	100	45	2.58	2.68	0.058	0.64	1.04
	150	48	3.03				
	200	50	3.35				
	250	53	3.88				
	300	54	4.06				
$AgGa_{0.95}In_{0.05}Ge_3Se_8$	100	51	3.52	2.65	0.068	0.63	1.06
	150	56	4.45				
	200	58	4.86				
	250	60	5.29				
	300	62	5.74				
$AgGaGe_{2.85}Sn_{0.15}Se_8$	100	60	5.29	2.58	0.078	0.62	1.08
	150	61	5.51				
	200	65	6.46				
	250	68	7.23				
	300	71	8.06				

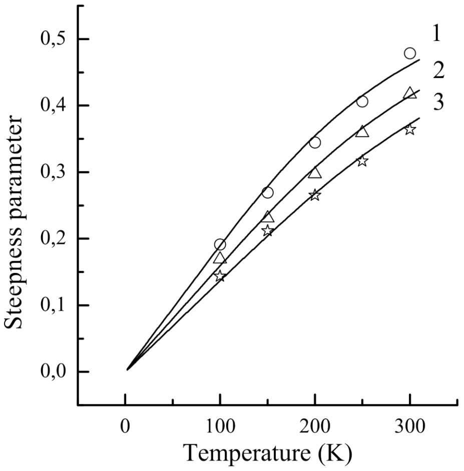


Fig. 4. Temperature dependence of the parameter σ for crystals of solid solutions $Ag_{0.95}Cu_{0.05}GaGe_3Se_8$ (*1*), $AgGa_{0.95}In_{0.05}Ge_3Se_8$ (*2*), and $AgGaGe_{2.85}Sn_{0.15}Se_8$ (*3*). Symbols correspond to experimental data, and solid curves to $\sigma(T)$-approximation functions

constant of the deformation potential. For semiconductors, in which the static disorder dominates, i.e. $\langle U^2\rangle_x \gg \langle U^2\rangle_T$, the function E_U is temperature-independent. In the case $\langle U^2\rangle_x \ll \langle U^2\rangle_T$, the dynamical disorder prevails,. It is related to thermal vibrations of atoms of the crystal lattice. For the considered crystals, the temperature dependence of E_U has a linear character, but the value of coefficient c ($c = dE_U/dT$) is different for different crystals. It is evident that the value of E_U at 100 K, i.e. when the contribution of the dynamical disorder is minimal, should be mainly determined by the statistical disorder. According to this criterion, the crystal of solid solution $AgGaGe_{2.85}Sn_{0.15}Se_8$, for which $c = 1.1 \times 10^{-4}$ eV/K, is the most imperfect, whereas the crystal of solid solution $Ag_{0.95}Cu_{0.05}GaGe_3Se_8$, for which $c = 1.4 \times 10^{-4}$ eV/K, is the most perfect. This fact can be explained as follows. At the statistical substitution of Ag atoms by Cu ones, easily diffusing Cu atoms can enter the crystal lattices and concentrate at various structural defects, which complex semiconductor compounds are always rich in [18]. For instance, it can be clusters of stoichiometric silver vacancies in compound's crystal lattice. In this case, Cu atoms can diminish the energy of elastic deformation fields around large structural defects and screen the electric fields of the space (bulk) charge around those defects.

Following the theoretical calculations presented in work [8] and using the experimentally determined value for E_U, we calculated the concentration n_t of charged defect centers that are responsible for the smearing of absorption edges in the researched compounds:

$$E_U = 2.2(n_t a_B^3)^{2/5} E_B,$$

where a_B and E_B are the Bohr radius and the Bohr energy, respectively. While calculating n_t, we consider that E_U is connected with a fluctuation in the concentration of single-charged point defects creating a stochastic electric field, which modulates the edges of allowed bands [7]. The obtained values are quoted in Table 3. It should be emphasized that the calculated value of concentration n_t for single-charged point defects (Table 3), which are responsible for the smearing of the absorption band edge, is practically three orders of magnitude lower than the concentration of vacancies V_{Ag}, which was determined from the X-ray diffraction researches of $AgGaGe_3Se_8$ crystal [7]. Provided that the concentration fluctuation of charged acceptors V_{Ag}^- is responsible for the smearing of the absorption band edge, we arrive at a conclusion that a considerable number of silver vacancies in the crystal lattice are in the neutral state, i.e. they are occupied by holes. It is not excluded that some of V_{Ag} vacancies can form neutral complexes, e.g., close donor-acceptor pairs $(V_{Ag}^- \text{-} D^+)^0$, where D^+ is a donor center of the impurity or intrinsic origin, for example, V_{Se}. Similar centers composed of intrinsic defects were observed in ternary chalcogenides $A_2B_2^3C_4^6$ ($CdGa_2S_4$ and $CdIn_2S_4$) [19].

In Fig. 4, the temperature dependence of the parameter σ is depicted, which was calculated from the experimental values, by using the relation

$$\sigma(T) = kT\frac{\Delta(\ln\alpha)}{\Delta(h\nu)}.$$

The symbols correspond to experimental data, and the solid curves to the $\sigma(T)$-approximation functions. The approximation of experimental results showed that the dependence $\sigma(T)$ is described well by the formula [20]

$$\sigma(T) = \sigma_0\frac{kT}{h\nu_0}\tanh\frac{h\nu_0}{2kT},$$

where $h\nu_0$ is the energy of phonons that interact with band electrons most effectively, and σ_0 is a constant related to the electron-phonon coupling strength g by the formula [21]

$$g = \frac{2}{3}\sigma_0^{-1}.$$

The determined approximation parameters are listed in Table 3. The obtained $h\nu_0$-values are larger than that for the highest optical mode in $AgInSe_2$ crystals (226 cm^{-1} or 28 meV [22]). Larger $h\nu_0$-values, if comparing with their analogs for ternary compounds, can be associated with structural frustrations induced by cation-cation substitutions, cation vacancies, implanted atoms, and deviations from the stoichiometry. The value $g > 1$ testifies to a strong electron-phonon coupling. The results obtained for the electron-phonon coupling strength are typical of crystals with stoichiometric defects in their cation sublattice [23, 24].

4. Conclusions

To summarize, the spectral distribution of the absorption coefficient in $AgGaGe_3Se_8$ single crystals doped with Cu, In, and Sn atoms has been studied in a temperature interval of 100–300 K. Using the value of light quantum energy at the absorption band edge (at $\alpha = 160\ cm^{-1}$), the energy gap width E_g in the compounds concerned is evaluated. The value of E_g is found to depend on the crystal lattice parameters. The temperature coefficient of the energy gap width variation is calculated to be $dE_g/dT = -(8.5 \div 9.5) \times 10^{-4}$ eV/K. For the researched crystals, the temperature dependence of E_U is found to have a linear character, with the corresponding slope dE_U/dT depending on the doping impurity. The concentration of charged defect centers n_t is calculated. The obtained g-value testifies to a strong electron-phonon coupling, which is typical of crystals with stoichiometric defects in their cation sublattice.

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ВПЛИВ ЛЕГУВАННЯ АТОМАМИ Cu, Sn I In НА ОПТИЧНІ ВЛАСТИВОСТІ МОНОКРИСТАЛІВ $AgGaGe_3Se_8$

Резюме

У роботі досліджено оптичні властивості монокристалів тетрарної фази $AgGaGe_3Se_8$, легованої атомами Cu, In, Sn. Ці сполуки є широкозонними напівпровідниками ($E_g \approx$ 2,15–2,09 еВ при T = 300 K) p-типу провідності з оптичними параметрами, які залежать від природи і концентрації легуючих домішок. На основі запропонованої фізичної моделі, з врахуванням особливостей невпорядкованих систем, проведено інтерпретацію одержаних експериментальних результатів.