ELECTRICAL AND OPTICAL PROPERTIES OF SOLID SOLUTIONS $Cu_{1-x}Zn_xInSe_2$ ($x = 0.05 - 0.2$)

V.V. BOZHKO, G.YE. DAVYDUYK, O.V. PARASYUK, O.V. NOVOSAD, V.R. KOZER

Lesya Ukrainka Volyn National University
(13, Volya Ave., Lutsk 43025, Ukraine; e-mail: novosadali@rambler.ru)

The temperature dependences of electroconductivity and the optical absorption edge in solid solutions of the system $CuInSe_2$–$ZnIn_2Se_4$ belonging to semiconductors with n-conductivity have been studied. The content dependence of the energy gap width in the solutions concerned has been found. The concentration dependences of the electromotive force coefficient, electron concentration, and Hall mobility of charge carriers have been determined.

1. Introduction

An important place among semiconducting substances is occupied by chalcogenide compounds with a diamond-like structure. In particular, they include ternary $A^I C^{III} X_2$ compounds which are derivative of $B^{II} X$ (X = S, Se) ones. Of late years, the interest in ternary chalcogenide compounds and their alloys has grown up [1]. In this work, solid solutions of the $CuInSe_2$–$ZnIn_2Se_4$ system were studied. The ternary compound $CuInSe_2$ and solid solutions on its basis are used as materials for thin-film heterojunctions in solar cells. However, their shortcoming is a narrow energy gap (E_g) which corresponds to the quantum energy in a spectral range far from the sunlight distribution maximum. The application scope of compounds of the given class can be extended by preparing and researching solid solutions in systems, where the second component is a compound with a similar structure and a wider energy gap.

Crystalline $CuInSe_2$ has a structure of the chalcopyrite type (the space group $I - \bar{4}2d$) with a cation–anion ordering that corresponds to the tetrahedral coordination of atoms in the crystal lattice. The cation-to-anion ratio in $ZnIn_2Se_4$ compounds, which are the second component (with a wider energy gap) of the solid solution under consideration, is 3:4. These materials are cation-defective, which is characteristic of $B^{II} C_2^{III} X_4$ compounds.

2. Preparation of Solid Solutions and Methods of Their Research

To find the regions of solid-phase solubility in the system $CuInSe_2$–$ZnIn_2Se_4$, we fabricated 21 specimens with a content step of 5 mol% $ZnIn_2Se_4$. High-purity elements (with a purity grade not less than 99.99 wt.%) were used for synthesis. Evacuated quartz ampoules filled with a blend were heated up in a shaft furnace to 1470 K. They were kept at this temperature for an hour and then cooled down to 870 K at a rate of $10-15$ K/h. The alloys obtained were annealed for 500 h. Afterward, they were hardened in cold water. The fabricated specimens were studied by x-ray phase analysis (an x-ray diffractometer DRON 4-13, CuK$_\alpha$ radiation). The elementary cell parameters were calculated using the PDWin 2 software package. The solid-solution ranges were determined by analyzing the variation of elementary cell parameters (Fig. 1). No intermediate phases were found in the system. The formation of solid solutions on the basis of components of the system concerned was found for the content intervals $0-22$ and $78-100$ mol% $ZnIn_2Se_4$ at the annealing temperature.

To study the mechanism of formation of the solid solutions under investigation, we used the method of x-ray diffraction analysis. As an example, the experimental, calculated, and difference diffraction patterns of alloy $Cu_{0.8}Zn_{0.2}InSe_2$ are shown in Fig. 2. A heterovalent substitution of copper atoms by zinc ones at the crystallographic position $4a$ was found. At the substitution, one atom of divalent zinc substitutes two atoms of univalent copper with the formation of tetrahedral voids, whose number is proportional to the number of zinc atoms in the emerged structure ($2Cu \longleftrightarrow Zn + \square$). Such a type of the formation of a solid solution gives rise to the appearance of cation-vacancy imperfections in the chalcopyrite structure, and the degree of this imperfection increases with the solid solution extension.

Hence, the features of the formation of a solid solution enable us to assert that zinc atoms available in the
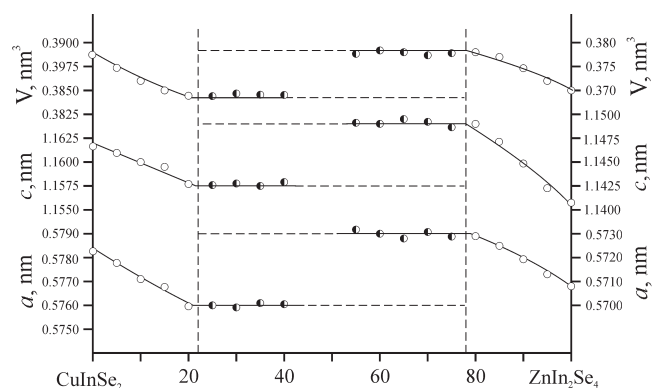
Fig. 1. Elementary cell parameters for various cross-sections of the CuInSe$_2$–ZnIn$_2$Se$_4$ system at 870 K

Fig. 2. Experimental, calculated, and difference diffraction patterns of the Cu$_{0.8}$Zn$_{0.2}$InSe$_2$ solid solution

solution structure have to affect the physical properties of compounds owing to the emergence of cation vacancies which are not observed in the chalcopyrite CuInSe$_2$ structure.

For the growing of solid-solution crystals on the basis of CuInSe$_2$, the horizontal variant of the Bridgman–Stockbarger method was chosen. Polycrystalline 8-g specimens of alloys, preliminarily synthesized of high-purity elements, were sealed in evacuated quartz ampoules with a conic end and placed into a furnace inclined at an angle of 10°. After the melts had been heated up to 1470 K, they were homogenized for 4 h. Then, the furnace was started to move with a velocity of 2 cm/day (the growth containers remained motionless). The temperature gradient at the crystallization front did not exceed 14 K/cm. After the crystals had achieved the isothermal zone at 870 K, they were annealed for 250 h and then cooled down to room temperature at a rate of 100 K/day. As a result, we obtained single crystals or blocks composed of single crystals with the dimensions suitable for physical experiments. Electric measurements were carried out using the specimens fabricated in the form of regular parallelepipeds $(3 - 8) \times (0.5 - 1) \times (1 - 2)$ mm^3 in size with deposited contacts made of indium or gallium-indium eutectic mixture. For optical measurements, we used crystals with plane-parallel surfaces of optical quality and $0.06 - 0.1$ mm in thickness or thin chips. At voltages below 10 V, all electric contacts had an Ohmic character. The specimen surfaces were mechanically polished using diamond pastes with various granular sizes.

Thermoelectric and electric properties were studied on standard installations in the dc signal mode. The light absorption coefficient (K) spectra were measured on a MDR-206 monochromator with a sensor on the basis of
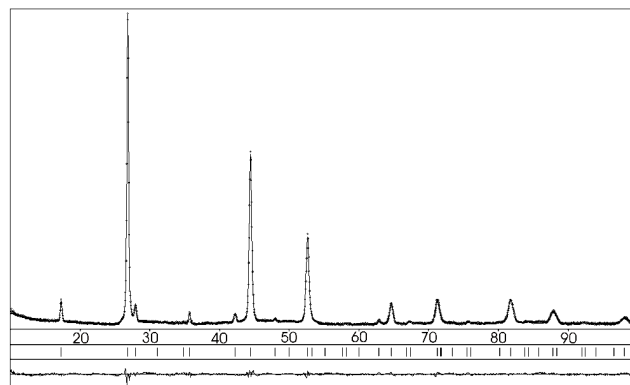
a silicon photodetector. The energy gap width E_g was estimated as the energy of light quanta $h\nu$, at which $K = 350$ cm^{-1} at the edge of the band of characteristic optical transitions.

3. Experimental Results and Their Discussion

It was found experimentally that the specific dark electroconductance σ of the crystals of solid solutions on the basis of CuInSe$_2$ compound decreases, if the content of the second component (ZnIn$_2$Se$_4$) increases (Fig. 3,a). According to the sign of thermo-emf coefficient, all specimens had conductivity of the n-type. The value of σ remained practically constant within the temperature interval $280 - 318$ K close to room temperature. A large value of $\sigma \approx (3.3 \div 3.6)$ Ω^{-1}cm^{-1} for solid solutions with the contents $5 - 10$ mol% ZnIn$_2$Se$_4$ (Fig. 3,a) and its temperature independence can testify that the corresponding state of crystals is close to a degenerate one. It should be noted that, in the CuInSe$_2$ case, the degeneration emerges at an electron concentration higher than 10^{17} cm^{-3} ($\sigma \approx (10^1 \div 10^2)$ Ω^{-1}cm^{-1}) [2], which agrees well with our results.

To determine the thermo-emf coefficient α, we took advantage of the relevant equation for degenerate semiconductors [2],

$$\alpha = \frac{k^2\pi^2 T}{3eE_f}\left(\frac{3r_0 + T}{r_0 + T}\right),\qquad(1)$$

where r_0 is a parameter independent of the temperature, and E_f is the Fermi level position. The calculated value $\alpha \approx 320$ μV/K turned out very close to that ($\alpha \approx 330$ μV/K) found experimentally for crystals with the content $5 - 10$ mol% ZnIn$_2$Se$_4$ at 292 K (Fig. 3,b).
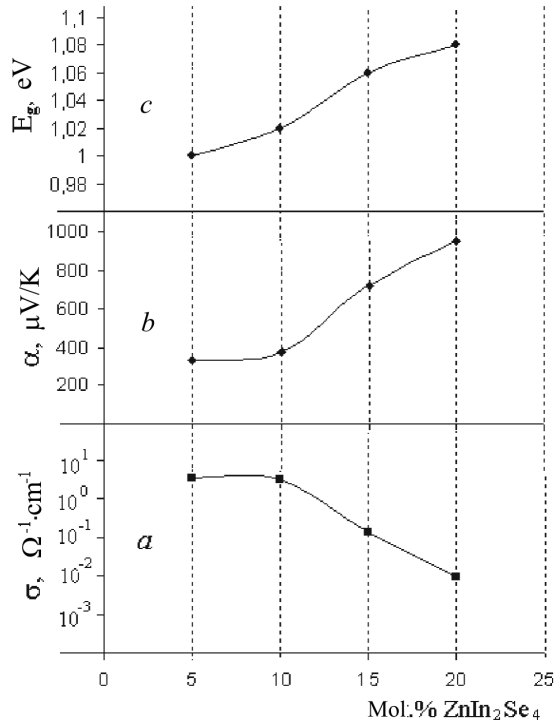
Fig. 3. Content dependences of (a) specific dark electroconductance, (b) thermo-emf coefficient, and (c) energy gap width of solid solutions of the $CuInSe_2$–$ZnIn_2Se_4$ system at 292 K

In this case, to put the theoretical and experimental α-values into agreement, we adopted that $r_0 = 20$ and $E_f = E_C - 0.05$. Such values of parameters r_0 and E_f turned out identical to their counterparts for degenerate $CuInSe_2$ films [2].

As is known [3], the figure of merit or the efficiency of a thermoelement is determined by the formula

$$Z = \frac{\alpha^2 \sigma}{\aleph}, \tag{2}$$

where $\aleph$ is the specific heat conductance. The latter consists of the lattice heat conductivity $\aleph_g$ and the electron heat conductivity $\aleph_e$:

$$\aleph = \aleph_g + \aleph_e. \tag{3}$$

In the first approximation, the heat conductivity of a crystal lattice $\aleph_g$ does not depend on the concentration of free charge carriers n, whereas $\aleph_e$ is proportional to n. To estimate the specific electron heat conductance, we took advantage of the equation describing $\aleph_e$ for degenerate semiconductors [4],

$$\aleph_e = \frac{\pi^2}{3e} k^2 \sigma T. \tag{4}$$

For our low-resistance alloys at 300 K, we obtained $\aleph_e \approx 2.8 \times 10^{-5}$ J/(s × cm × K). According to the data of work [5], the specific heat conductance of the $CuInSe_2$ single-crystal lattice amounts to $\aleph_g \approx 2.9 \times 10^{-2}$ J/(s × cm × K), i.e. $\aleph_e/\aleph_g \approx 10^{-3}$.

It should be noted that similar results are valid for other heavily doped semiconductors as well [6]. For instance, for n-silicon with a donor concentration of 8×10^{19} cm^{-3}, the ratio $\aleph_e/\aleph_g \approx 6 \times 10^{-3}$. Therefore, we may assert that, for the studied crystals,

$$\aleph = \aleph_g. \tag{5}$$

Taking the aforesaid into account, we obtained $ZT \approx 4 \times 10^{-3}$ for crystals with the contents of $5 - 10$ mol% $ZnIn_2Se_4$ in the range of room temperatures. For alloys with higher contents of $ZnIn_2Se_4$, the ZT-value is lower.

Hence, crystals of solid solutions on the basis of $CuInSe_2$ have a high α-value, and they can be used as materials for sensitive thermal sensors. At the same time, they are not promising materials for thermoelectric generators, for which the value of ZT falls within the interval $0.1 - 1$.

The increase of the $ZnIn_2Se_4$ content in the alloys concerned is accompanied by a decrease of their σ (Fig. 3,a). This can be related to an increase of the energy gap width E_g (Fig. 3,c). At 292 K, the latter is equal to 0.86 eV for $CuInSe_2$ [7] and about 2 eV for $ZnIn_2Se_4$ [5]. In the alloys, a certain role is played by the variation of their defect structure. As was indicated above, the increase of the Zn content gives rise to the concentration growth of cation vacancies which play the role of acceptor centers.

The study of the Hall effect enabled us to determine the concentration n and the mobility μ of majority charge carriers for specimens (see Table 1). In work [5], the value $\mu \approx 1000$ cm^2/(V × s) was reported for the Hall mobility of charge carriers in a $CuInSe_2$ single crystal. A low value of μ for electrons in the alloys (Table 1) testifies to a high imperfection of the latter, which confirms a conclusion drawn earlier. Moreover, the high imperfection of the crystals under consideration, in turn, is evidently responsible for their low photosensitivity.

Table 1. Key parameters of $CuInSe_2$–$ZnIn_2Se_4$ alloys at $T \approx 292$ K

mol%, $ZnIn_2Se_4$	E_g, eV	R, cm^3/C	n, cm^{-3}	μ, cm^2/V·s	σ, $(\Omega \cdot cm)^{-1}$	α, $\mu V/K$
5	1	19.3	$3.82 \cdot 10^{17}$	59	3.6	330
10	1.02	13.3	5.56×10^{17}	37	3.3	370
15	1.06	1097	6.72×10^{15}	130	0.14	720
20	1.08	8760	8.40×10^{14}	70	9.2×10^{-3}	950
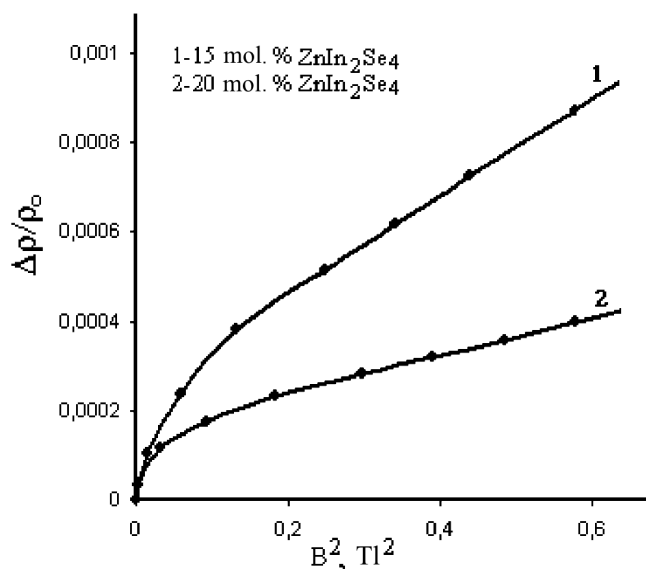
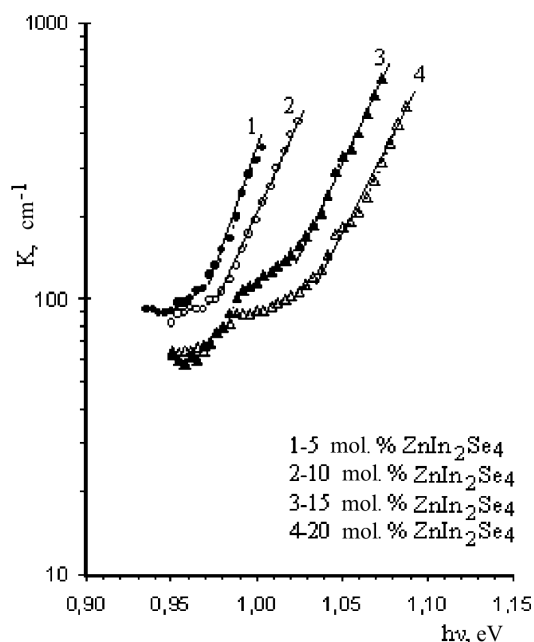Fig. 4. Dependences of the transverse magnetoresistance $\Delta\rho/\rho_0$ on the magnetic induction

Fig. 5. Energy distributions of the light absorption coefficient in solid solutions $CuInSe_2$–$ZnIn_2Se_4$ at 292 K

Magnetoresistance researches of nondegenerate specimens led to approximately the same values of electron mobility. In Fig. 4, the dependences of the transverse magnetoresistance of specimens on the magnetic field induction at 292 K are given. In a broad field interval, the relative variation of the magnetoresistance is described well by the square-law dependence [8]

$$\Delta\rho/\rho_0 = \mu^2 B^2 (C - A^2). \tag{6}$$

In order to put the experimental results in agreement with formula (6), we took $C - A^2 \approx 7$, which is close to the characteristic value obtained at the electron scattering by ionized impurities [8]. For degenerate specimens, we did not succeed in measuring their magnetoresistances owing to their very small values.

In Fig. 5, the energy dependences of the light absorption coefficient $K(\nu)$ near the edge of own optical transitions (EOOT) in the crystals concerned are presented. As follows from the figure, the dependence $K(\nu)$ is described well by the Urbach rule [9], which testifies that

T a b l e 2. **Parameters of the characteristic absorption band edge of solid solutions** $CuInSe_2$–$ZnIn_2Se_4$ **at** $T \approx 292$ **K**

Specimen No.	mol%, $ZnIn_2Se_4$	Δ_0, eV	E_g, eV
1	5	0.028	1.00
2	10	0.030	1.02
3	15	0.034	1.06
4	20	0.036	1.08

the tails of the density of states, stemming from the crystal lattice imperfection, take part in the formation of optical transitions:

$$K(\nu) \sim \exp\left(-\frac{E_{g0} - h\nu}{\Delta_0}\right), \tag{7}$$

where E_{g0} is a constant proportional to the energy gap width at 0 K; and Δ_0 is a characteristic energy which determines a degree of the EOOT smearing, being a criterion of the crystal lattice disordering.

The values of Δ_0 determined for specimens with various contents from the experimental dependence (7) are listed in Table 2. A large Δ_0-value, close to that in disordered semiconductors [10], evidences for a high imperfection of compounds which grows (it is reflected by the growth of Δ_0) with increase in the $ZnIn_2Se_4$ content. Such a behavior agrees well with a conclusion made earlier on an increase of the cation vacancy concentration in the crystals of solid solutions on the basis of $CuInSe_2$ with increase in the second component content.

As is known [9], there is a relation between Δ_0 and the concentration of charged point defects n_t responsible for the absorption edge smearing, which is expressed by the formula

$$\Delta_0 = 2,2\left(n_t a_b^3\right)^{2/5} E_b, \tag{8}$$

where $a_b = \varepsilon\hbar^2/me^2$ is the Bohr radius of an electron, and $E_b = m_e e^4/2\varepsilon^2\hbar^2$ is the Bohr energy. Making use of the experimentally determined Δ_0-value, we evaluated n_t for single-charged centers. In so doing, we assumed the parameter $\varepsilon \approx 11.6$ and the effective electron mass $m_e \approx 0.2m_0$ to be the same as that in the single crystals of ZnSe which is an analog of ternary compounds. We obtained the values of n_t falling within the interval $(1 \div 3) \times 10^{19}$ cm^{-3} for various specimens.

The crystals under investigation are characterized by a considerable light absorption in the range adjacent to EOOT (Fig. 5). Such an absorption of light is caused by large-scale defects in the crystal lattice which generate potential relief perturbations: dislocations, defect aggregations, twin boundaries, and others [11]. Such a phenomenon may testify to the existence of large defect complexes responsible for the near-edge absorption and the dispersion of light which reduce the crystal transparency in this spectral range. It should be noted that some authors [5] arrived at the conclusion on the existence of large complexes formed by anions around cation vacancies in $A^{II}B_2^{III}C_4^{IV}$ compounds.

4. Conclusions

Solid solutions $CuInSe_2$–$ZnIn_2Se_4$ belong to semiconductors with conductivity of the n-type. A high imperfection makes them closer to disordered systems, which manifests itself in some features of electric and optical parameters of those compounds. The energy gap width in $CuInSe_2$–$ZnIn_2Se_4$ compounds and its dependence on the component content have been determined. Within the limits of the existence of a homogeneous solid solution, the gap width was demonstrated to grow smoothly with increase in the second component content (with a wider energy gap). The dependences of the electron concentration and the electron Hall mobility on the solution content have been found.

1. V.B. Lazarev, Z.Z. Kim, E.Yu. Peresh, and E.E. Semrad, *Complex Chalcogenides of the Systems A^I-B^{II}-C_2^{VI}* (Metallurgiya, Moscow, 1993) (in Russian).

2. A. Amara, A. Drici, and M. Guerioune, Phys. Status Solidi A **2**, 195 (2003).

3. V.V. Pasynkov, L.K. Chirkin, and A.D. Shishkov, *Semiconductor Devices* (Vysshaya Shkola, Moscow, 1973) (in Russian).

4. A.I. Anselm, *Introduction to Semiconductor Theory* (Prentice-Hall, Englewood Cliffs, NJ, 1981).

5. N.A. Goryunova, *Complex Diamond-Like Semiconductors* (Sovetskoe Radio, Moscow, 1968) (in Russian).

6. V.I. Fistul, *Heavily Doped Semiconductors* (Plenum Press, New York, 1969).

7. P.I. Baranskii, V.P. Klochkov, and I.V. Potykevich, *Semiconductor Electronics. Reference Book* (Naukova Dumka, Kyiv, 1975) (in Russian).

8. P.S. Kireev, *Semiconductor Physics* (Mir Publishers, Moscow, 1978).

9. V.L. Bonch-Bruevich, R. Enderlein, B. Esser, R. Keiper, A.G. Mironov, and I.P. Zvyagin, *Elektronentheorie Ungeordneter Halbleiter* (Wissenschaften, Berlin, 1984).

10. I.A. Vainshtein, A.F. Zatsepin, V.S. Korotov, and Yu.V. Shchapova, Fiz. Tverd. Tela **42**, 2 (2000).

11. N.R. Kulish, M.P. Lisitsa, M.I. Malysh, and B.M. Bulakh, Fiz. Tekh. Poluprovodn. **24**, 1 (1990).

ВИГОТОВЛЕННЯ, ЕЛЕКТРИЧНІ ТА ОПТИЧНІ
ВЛАСТИВОСТІ ТВЕРДИХ РОЗЧИНІВ
$Cu_{1-x}Zn_xInSe_2$ $(x = 0,05 - 0,2)$

В.В. Божко, Г.Є. Давидюк, О.В. Парасюк, О.В. Новосад, В.Р. Козер

Р е з ю м е

Тверді розчини системи $CuInSe_2$–$ZnIn_2Se_4$ належать до напівпровідників n-типу провідності. Досліджено їх температурні залежності електропровідності та край оптичного поглинання. Визначено ширину забороненої зони твердого розчину системи $CuInSe_2$–$ZnIn_2Se_4$ залежно від складу. Також встановлено концентраційну залежність коефіцієнта термо-ерс, концентрації електронів і холлівську рухливість носіїв заряду.