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Nonstoichiometry of CuInSe_2 and method of controlled atomic defects

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Abstract

The results of a complex study of the crystal structure, mechanical, galvanomagnetic and thermoelectric properties of CuInSe_2 under different schemes and degrees of deviation from stoichiometry are presented. Nonstoichiometric compositions for studies were selected using the method of 'controlled atomic defects'. The solubility limits of extrastochiometric dopants (Se, CuIn, InSe, CuSe_2 , InSe_2 and In_2Se_3) are determined, and the types of predominant intrinsic defects corresponding to different schemes of deviation from stoichiometry are identified. On the basis of the temperature dependences of the galvanomagnetic properties, positions of energy levels created by nonstoichiometric defects of different types (Cu, In and Se vacancies, Cu_{In} and In_{Cu} substitution defects, Se interstitials) are determined. The correlation between composition, type and concentration of nonstoichiometric defects, structure and properties of CuInSe_2 under various modes of deviation from stoichiometry is established.

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1. Introduction

Comprehensive study of the CuInSe_2 (CIS) semiconducting compound, a most promising material for solar cell energy applications [1–3], is still of a great interest nowadays.

One of the most effective methods of controlling properties of this material is deviation from stoichiometry, which makes it possible not only to vary its physical parameters in a wide range but also to change the dominant charge carrier sign. However, so far, the problems of unambiguous identification of nonstoichiometric defects and establishment of the composition–property relationships are far from solution [4–8]. A wide spectrum of intrinsic defects coexisting in CIS complicates solving these problems. That is why we propose to use the method of 'controlled atomic defects', which allows us to introduce intrinsic defects of a desired type into

the crystal and vary the defect concentration by moving along a definite section of the Cu–In–Se concentration triangle that passes through the CuInSe_2 compound.

The application of the method of controlled atomic defects to the CIS ternary compound gives a possibility to vary the defect structure in different ways and to establish the influence of defects of different types on the CIS structure and properties. For example, moving along the CIS–Se section allows us to introduce into CIS mainly cation vacancies (V_{Cu} and V_{In}) or Se interstitials (Se_i). Changing composition along the CIS– InSe_2 and CIS– CuSe_2 sections, we can introduce V_{Cu} or V_{In} , respectively, whereas doping CIS with extrastochiometric In_2Se_3 (the Cu_2Se –CIS– In_2Se_3 section) leads to the simultaneous introduction of In_{Cu} substitution defects and cation vacancies V_{Cu} . When doping CIS with CuSe and InSe (the CIS– CuSe and CIS– InSe sections), we introduce with the highest probability Cu_{In} and In_{Cu} substitution defects, respectively. Certainly, other mechanisms of defect formation are also possible, but comparing formation energies for different types of defects, one can predict the most

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probable defect structure for a certain scheme of deviation from stoichiometry.

Below the results of the examination of the CIS crystal structure and physical properties along different sections in the Cu–In–Se triangle are presented.

2. Experimental

Polycrystalline samples were prepared by direct melting of high-purity components in evacuated down to $\sim 10^{-3}$ Pa quartz ampoules at 1380 ± 10 K, and subsequent homogenizing annealing at 920 ± 10 K during 200 h. The composition of each sample was controlled using chemical analysis as well as X-ray spectroscopy, which showed that deviation of chemical composition from the nominal value did not exceed ± 0.03 at.% for each element. Mass spectrometry did not reveal any additional impurities in the studied samples. Selective local X-ray spectroscopy analysis as well as precise determination of unit cell parameters, local measurements of microhardness, microthermo-e.m.f. and electrical conductivity in different parts of ingots were used to examine the samples homogeneity. As a rule, scatter in values of those parameters did not exceed the errors of their determination. The lattice parameters a and c were determined with an accuracy of $\Delta a = 2 \times 10^{-4}$ Å and $\Delta c = 4 \times 10^{-4}$ Å using DRON-2 diffractometer and Ni-filtered Cu K_{α} -radiation. Microstructure examination was carried out on freshly polished sections etched in a 10:1 mixture of saturated aqueous $K_2Cr_2O_7$ solution and concentrated H_2SO_4 . Microhardness H was measured using a PMT-3 tester at applied load of 0.49 N. The root mean square error for a series of measurements (30–50 indents for each sample) did not exceed $\pm 3\%$. The electrical conductivity σ and the Hall coefficient R_H were determined in the temperature range of 80–300 K using a conventional direct-current method and in a magnetic field of ~ 1 T. The error of R_H and σ determination was $\sim 5\%$. The charge carrier mobility μ_H was calculated as $\mu_H = \sigma R_H$ and the charge carrier concentration was determined assuming the Hall factor to be 1. The Seebeck coefficient S was determined with regard to Cu with an accuracy of not less than 3%.

3. Results and discussion

In Fig. 1, the Cu–In–Se concentration triangle, in which we show sections studied in the present work (a), and the range of investigated compositions in the vicinity of the CIS compound (b) are presented.

Under excess of Se relative to the stoichiometric composition at the fixed cation ratio $[Cu]/[In] = 1$ (section 1, Fig. 1a), the concentration dependences of a , c [9], H and the width of diffraction lines B (Fig. 2) behave in a complex

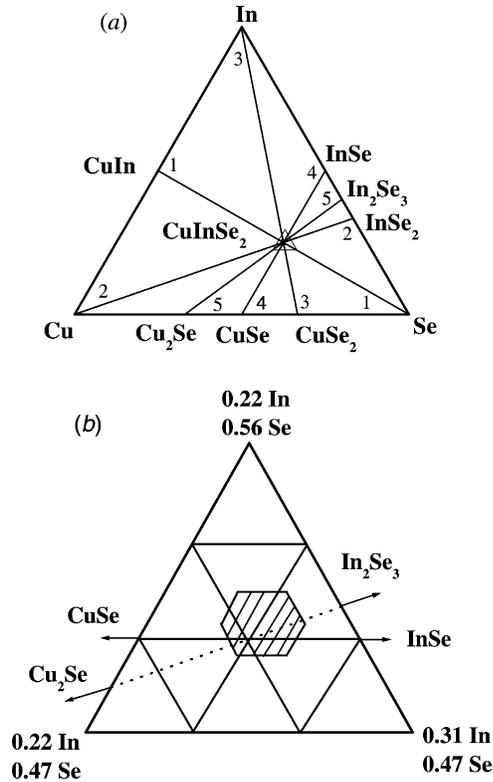


Fig. 1. The Cu–In–Se concentration triangle (a) with sections studied in this work (1–5) and the range of studied composition shown by the shaded region (b).

manner within CIS homogeneity region (49.9–51.0 at.% Se [10]) exhibiting the minimum in the vicinity of ~ 50.5 at.% Se. The decrease in a and c observed in CIS with increasing Se concentration in Ref. [9] was attributed to the appearance of V_{Cu} and V_{In} , whose concentration in the cation sublattice at ~ 50.5 at.% Se reaches ~ 2 at.% under condition of their predominant formation. Such a high concentration of defects inevitably leads to their interactions (electrostatic,

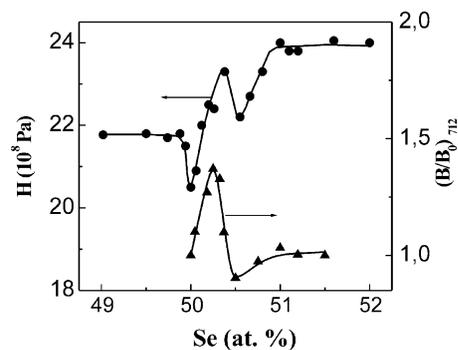


Fig. 2. Microhardness and width of diffraction lines vs. Se content in the CIS–Se system.

deformational, etc.). When such interactions occur, the overlapping of the elastic fields of separate defects may result in at least partial compensation of stresses of opposite sign [11] and, thus, cause a drop in H , which was actually observed in the vicinity of ~ 50.5 at.% Se (Fig. 2). Further formation of vacancies (more than ~ 2 at.%) may become thermodynamically unfavorable, and a change in the defect formation mechanism will take place (for example, generation of Se interstitials and/or antisite defects). The increase in the unit cell parameters above ~ 50.5 at.% Se [9] supports this supposition.

The presence of extrema in the composition–property dependences allows us to suggest the possibility of ordering of cation vacancies when their concentration is high. The probability of defect redistribution grows significantly for electrically active defects [12]. The estimation of optimal compositions for ordering shows that within the CIS homogeneity region in the CIS–Se system, several variants of cation vacancies ordering are possible. At ~ 50.5 at.% Se, the formation of a fcc vacancy sublattice with a parameter $a_v = 4a$ and the shortest distance between vacancies $d_v = 2.8a$ (where a is the CIS unit cell parameter) is most likely. The decrease in B in the range of 50.25–50.5 at.% Se (Fig. 2) indicates a reduction in the degree of lattice distortion during the introduction of nonstoichiometric defects and confirms our supposition about vacancy ordering.

The increase in the hole concentration with increasing concentration of extrastochiometric Se as well as the drop in μ_H and σ [13] are in good agreement with an increase in the concentration of cation vacancies (V_{Cu} and V_{In} with activation energies of ~ 20 and 70 meV, respectively [13]) playing role of acceptors. The deeper acceptor level may also be connected with Se_i . This is confirmed by the increase in a and c in the range of ~ 50.5 –51 at.% Se.

The inversion of dominant charge carrier sign from p to n under Se deficit in CIS [10] is in good agreement with predictions on the basis of the method of controlled atomic defects about the formation of donor-like defects (V_{Se} and Cu and In interstitials under Se deficit). Taking into consideration an increase in the unit cell parameters under Se deficit [9], energies of the defect formation [8, 14] and a high migration ability of Cu atoms, one can attribute the detected on the basis of the $R_H(T)$ dependence donor level to Cu_i defects which coexist with V_{Se} .

The behavior of the concentration dependences of properties (a , c , H , σ , R_H , S) and the results of the microstructural analysis of CIS–InSe₂ alloys (section 2 in Fig. 1) indicate that the solubility of InSe₂ in CIS does not exceed ~ 1.5 mol%. A decrease in the unit cell parameters with increasing nonstoichiometric defect concentration confirms the supposition about the formation of V_{Cu} . As is seen from Fig. 3, all the samples doped with InSe₂ exhibit p-type conductivity, while under deficit of InSe₂, an inversion

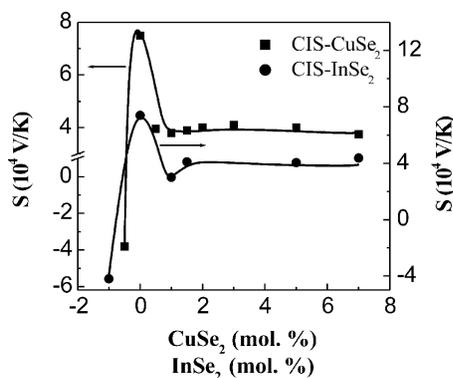


Fig. 3. Concentration dependence of the Seebeck coefficient in the CIS–CuSe₂ and CIS–InSe₂ systems.

of the dominant carrier sign from p to n is observed. The appearance of an acceptor level with the activation energy of ~ 70 meV is attributed to Se_i defects, which can coexist with V_{Cu} .

The Seebeck (Fig. 3) and the Hall coefficient measurements showed that all the samples doped with CuSe₂ (section 3, Fig. 1) manifest p-type conductivity, while under deficit of CuSe₂ relative to the CIS stoichiometric composition, an inversion of the dominant carrier sign from p to n occurs. A donor level with the activation energy of ~ 70 meV was detected on the basis of the temperature dependence of R_H . This value of the defect activation energy is in good agreement with that obtained for CIS with Se excess.

It is shown that Cu \rightarrow In substitution under the fixed Se concentration (50 at.%) in CIS (section 4, Fig. 1) leads to an increase in a , c , and H [9,15] and to an inversion of the dominant carrier sign from p to n already when the first portions of defects are introduced (Fig. 4). The limits of the homogeneity region in the CIS–InSe system are determined to be ~ 1.5 –2 mol% [9,15]. The estimation of the concentration dependence of a in the approximation of Vegard's law confirms our suggestion about the In_{Cu}

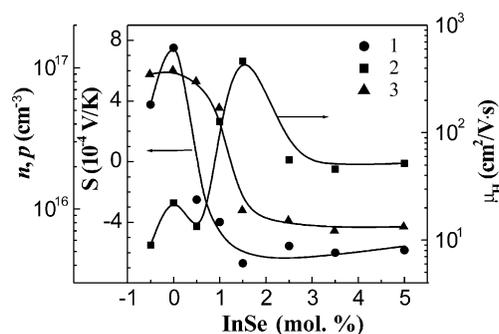


Fig. 4. Room temperature dependences of the Seebeck coefficient (1), charge carrier mobility (2), and charge carrier concentration (3) on InSe content in the CIS–InSe system.

defect formation based on the method of controlled atomic defects. From the temperature dependences of R_H , a donor level attributed to In_{Cu} with the energy of ~ 30 meV was found.

As is seen from Fig. 4, an unexpected decrease in the charge carrier concentration (down to $\sim 10^{16} \text{ cm}^{-3}$) and a simultaneous increase in the electron mobility (up to $\sim 470 \text{ cm}^2/\text{V s}$) are observed when extrastochiometric InSe (up to $\sim 1.5\text{--}2$ mol%) is introduced into CIS. Since InSe is a stable compound, with increasing deviation from stoichiometry corresponding to the introduction of equal amounts of In and Se atoms into CIS, the probability of the formation of electrically neutral InSe complexes increases. It stimulates the processes of recharging ($\text{In}^{+3} \rightarrow \text{In}^{+1}$) when InSe concentration increases. Taking into account that In atoms exist in different valence states (In^{+3} and In^{+1}) [16], the decrease in the charge carrier concentration can be connected with growing number of In atoms participating in the formation of InSe neutral complexes. An increase in μ_H in the range of 0 to 1.5–2 mol% InSe (Fig. 4) is quite expected and can be associated with decreasing number of scattering centers in the crystal lattice due to the formation of neutral complexes. The observed effect allows us to obtain optimal, for solar cell applications, values of the charge carrier concentration in CIS ($10^{16}\text{--}10^{17} \text{ cm}^{-3}$) and a high charge carrier mobility by introducing extrastochiometric InSe, and shows one of the ways for improving characteristics of CIS-based devices.

The substitution $\text{In} \rightarrow \text{Cu}$ upon introduction of CuSe into CIS does not change the dominant carrier sign (p-type), and an increase in a , c and H is observed. The existence of an acceptor level with the energy of ~ 37 meV in the sample doped with CuSe is attributed to Cu_{In} substitution defects, which are the most probable defects under this scheme of deviation from stoichiometry. An increase in the lattice parameters, which we observed in Refs. [9,15], can be connected with the location of at least of part of Cu atoms in interstices.

Moving along the quasi-binary CIS– In_2Se_3 section separating the ranges with p- and n-type conductivity in the Cu–In–Se concentration triangle (section 5 in Fig. 1) corresponds with the highest probability to the following defect formation scheme: $3\text{Cu} \rightarrow \text{In}_{\text{Cu}} + 2V_{\text{Cu}}$, where V_{Cu} is the neutral vacancy. It is found that all studied samples (along section 5) manifest p-type conductivity. The limit of solubility of In_2Se_3 in CIS is at least 8 mol%. The decrease in a , c and in H and the sharp growth in the charge carrier concentration (Fig. 5) are observed when the first portions of the extrastochiometric dopant (up to ~ 1 mol% In_2Se_3) are introduced. The drop in the unit cell parameters is attributed to the predominant influence of cation vacancies, which are caused by the introduction of In_2Se_3 and have a smaller effective radius in comparison with those of Cu and In. On the basis of

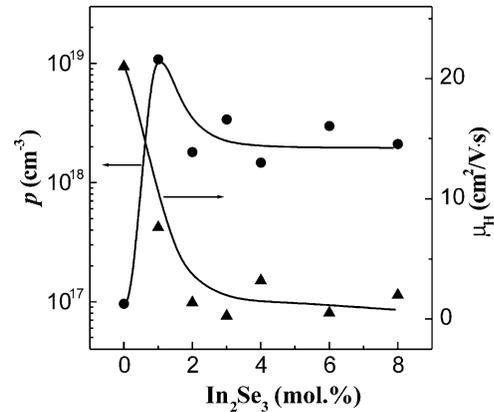


Fig. 5. Room temperature dependences of the charge carrier concentration and charge carrier mobility on In_2Se_3 content in the CIS– In_2Se_3 system.

the temperature dependences of the galvanomagnetic properties, a shallow acceptor level probably caused by V_{Cu} defects is detected.

Another interesting peculiarity of CIS properties modification caused by doping with In_2Se_3 is an abrupt change in p , μ_H , σ , and S when the first portion of dopant (up to ~ 1 mol% In_2Se_3) are introduced and the constancy of p , μ_H , and σ within the homogeneity region under further introduction of the dopant. Thus, there exists only a narrow range of acceptor-like electrical action of dopant. One can suppose that when deviation from stoichiometry is small, the substitution scheme $3\text{Cu} \rightarrow \text{In}_{\text{Cu}} + 2V_{\text{Cu}}$ is not realized yet. In this case, an increase in p can be associated with increasing concentration of cation vacancies whose charge is not compensated due to simultaneous introduction of In. On the other hand, the introduction of the first portions of cation vacancies in the absence of interactions between them stimulates recharging of In atoms ($\text{In}^{+3} \rightarrow \text{In}^{+1}$), thus decreasing their electrical activity. A similar effect of recharging of In atoms was observed upon introduction of In into SnTe [16].

The constancy of p , μ_H , and σ within the homogeneity region at In_2Se_3 concentrations higher than ~ 1 mol% is attributed to the formation of electrically neutral complexes at higher degrees of deviation from stoichiometry.

4. Conclusions

The complex study of the crystal structure, mechanical, galvanomagnetic and thermoelectric properties of CuInSe_2 crystals under different schemes and degrees of deviation from stoichiometry was performed. The method of controlled atomic defects was used for intentional introduction of nonstoichiometric defects of a desired type into CuInSe_2 . The correlation between composition, type and concentration of nonstoichiometric defects, structure and physical

properties was established. On the basis of microstructural and X-ray diffraction analyses, the limits of the CIS homogeneity region along different sections in the Cu–In–Se ternary system were determined. It was shown that the maximum solubility is observed along the CIS–In₂Se₃ section.

When extrastochiometric Se is introduced into CIS, a change in defect formation mechanism takes place at the Se concentration exceeding 50.5 at.%. The presence of extrema in the composition–property dependences in the vicinity of the indicated concentration allows us to assume the possibility of ordering of cation vacancies at their high concentrations. Optimal compositions for the ordering are estimated.

It was found out that when deviation from stoichiometry corresponds to the introduction of a stable compound (InSe, In₂Se₃), only the first portions of dopant produce electrical action (donor or acceptor, respectively), which is attributed to the formation of electrically neutral complexes at higher degrees of deviation from stoichiometry.

The results obtained in this work prove fruitfulness of using the controlled atomic defects method for the development of physical foundations of controlling properties of complex semiconductor phases by introducing nonstoichiometric defects.

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