Preparation and Phase Relations in the CuSbSe₂ – CuInSe₂ System

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ABSTRACT

The CuInSe₂ and CuSbSe₂ ternary compounds and alloys of the (CuSbSe₂)₁₋ₓ(CuInSe₂)ₓ system with the mole fraction of CuInSe₂ (x) equal to 0.05, 0.15, 0.25, 0.375, 0.50, 0.625, 0.75, 0.85, and 0.95 were prepared and the phase relations in this system were investigated by X-ray powder diffraction, optical microscopy, and scanning electron microscopy. It was shown that the alloys of the CuSbSe₂-CuInSe₂ system are biphasic at room temperature in the whole range of compositions, and the limits of solubility for CuSbSe₂ in CuInSe₂ and for CuInSe₂ in CuSbSe₂ do not exceed 0.001 mole fraction.

INTRODUCTION

Copper indium diselenide (CuInSe₂) belongs to the I-III-VI₂ group compounds and is extensively studied and used as an absorbing material in solar cells, especially with the combination of CuGaSe₂ compound with which it forms promising CIGS compounds. CIGS-based solar cells have the third largest market, following Si- and CdTe-based solar cells [1]. One of the methods to optimize physical properties of these compounds is to improve the procedure of doping. Chemical elements of the group 15 (As, Sb, Bi) can be used as doping elements; moreover, CuSbSe₂, CuSbSe₂, CuBiSe₂, and CuBiSe₂ themselves are studied as potential photovoltaic materials [2, 3]. Previously, the (CuBiSe₂)₁₋ₓ(CuInSe₂)ₓ [4] and (CuSbSe₂)₁₋ₓ(CuInS₂)ₓ [5] alloys were prepared and the phase relations in these systems above 600 K were investigated by X-ray powder diffraction, microstructure studies, and differential thermal analysis. It was established that the T-x phase diagram of the CuInSe₂-CuBiSe₂ system has a peritectic character with a peritectic temperature of 837 K [4]. The limits of solubility from both sides of the system do not exceed 0.05 mole fraction of the corresponding ternary compounds. By contrast, the T-x phase diagram of the CuInSe₂-CuBiSe₂ system has a eutectic character with a eutectic temperature of 807 K [5]. The alloys of the CuSbSe₂-CuInS₂ system where the mole fraction of CuInS₂ ranged from 0.038 to 0.941 are biphasic at room temperature, and the limits of solubility are 0.059 mole fraction for CuSbSe₂ in CuInS₂ and 0.038 mole fraction for CuInS₂ in CuSbSe₂.

To perform successful doping of CuInSe₂ by antimony, the phase relations in the Cu-Sb-Se system have to be known. To date, the knowledge of the Cu-Sb-Se system is rather scarce and contradictory. In the previous studies this system was experimentally studied only across the Cu₂Se-Sb₂Se₃ [6] and Cu₀.₇₅Sb₀.₂₅-Se [7] intersections. The phase diagram of the Cu₂Se-Sb₂Se₃
system in the whole series of compositions was constructed and the formation of only one ternary compound with the chemical composition CuSbSe$_2$ was found [6]. Its melting has a congruent character with a melting point of 763 K. This is in contradiction with previous findings [8], in which the second ternary compound in the Cu$_2$Se-Sb$_2$Se$_3$ system with the composition of Cu$_3$SbSe$_2$ was prepared. One more compound of the Cu-Sb-Se system—Cu$_3$SbSe$_4$—was first synthesized separately [9] and its phase diagram indicates that this material forms via a peritectic reaction at about 663 K [7]. Its crystal structure was also established [10, 11]. Recently, in addition to CuSbSe$_2$, Cu$_3$SbSe$_3$, and Cu$_3$SbSe$_4$ compounds, prediction of the new stable, previously unknown in the Cu-Sb-Se system, compounds Cu$_4$SbSe$_5$ and Cu$_{12}$Sb$_4$Se$_{13}$, was made [12].

To determine the homogeneity region of CuSbSe$_2$, the alloys (Cu$_2$Se)$_{1-x}$ (Sb$_2$Se$_3$)$_x$ in the range of x from 0.485 to 0.515 were studied [13]. It was found that at the eutectic temperatures (750 and 744 K) the range of homogeneity of CuSbSe$_2$ is 0.0088 mole fraction, and the solubility of Cu$_2$Se in CuSbSe$_2$ is 0.0068 mole fraction and the solubility of Sb$_2$Se$_3$ in CuSbSe$_2$ is 0.0020 mole fraction. The homogeneity range of CuSbSe$_2$ at 298 K does not exceed 0.0060 mole fraction. A maximal melting point (764 K) is shifted to Cu$_2$Se and corresponds to the composition (Cu$_2$Se)$_{0.496}$ (Sb$_2$Se$_3$)$_{0.504}$. An alloy with the stoichiometric composition CuSbSe$_2$ melts at 754 K.

The crystal structure of CuSbSe$_2$ was studied on thin films and was found to be an orthorhombic structure with the space group Pnma and the lattice constants 6.400, 3.950, and 15.33 Å for a, b, and c, respectively [14]. It was determined that the lattice constants for CuSbSe$_2$ prepared by solid state reaction from elements are 6.303, 3.976, and 15.008 Å for a, b, and c, respectively [15]. A low temperature solvothermal method was used for the preparation of CuSbSe$_2$ and the crystal structure was determined using single crystal X-ray diffraction analysis to be an orthorhombic structure with the space group Pnma and the lattice constants 6.299, 3.9734, and 15.005 Å for a, b, and c, respectively [16].

The absence of the complete formation of solid solutions was found when the (CuSbSe$_2$)$_{1-x}$ (CuInSe$_2$)$_x$ alloys were prepared for the first time [15]. Then the doping of CuInSe$_2$ by Sb in the CuIn$_{1-x}$Sb$_x$Se$_2$ for x=0.0025, 0.005, and 0.010 was developed [17]. By introduction of CuSbSe$_2$ doping into CuInSe$_2$, the well-crystallized ceramic samples can be perfectly sintered at 773 K.

Considering that the best way of determination of solubility of antimony in CuInSe$_2$ and indium in CuSbSe$_2$ is to study phase equilibria in the CuInSe$_2$-CuSbSe$_2$ system, the goal of the present paper was to prepare and study the microstructure of alloys and phase relations in the CuSbSe$_2$-CuInSe$_2$ system and to determine the limits of solubility.

**EXPERIMENT**

Nine alloys of the (CuSbSe$_2$)$_{1-x}$ (CuInSe$_2$)$_x$ system with the mole fraction of CuInSe$_2$ (x) equaling 0.05, 0.15, 0.25, 0.375, 0.50, 0.625, 0.75, 0.85, and 0.95 and pure CuSbSe$_2$ and CuInSe$_2$ compounds were prepared. The initial elements for the preparation of the alloys and CuInSe$_2$ (x=1) ternary compounds were 99.9998% copper, 99.9997% indium, 99.999 antimony, and 99.9999% selenium. The required amounts of the corresponding chemical elements were weighed and sealed in evacuated quartz ampules. Samples of the alloys and ternary compounds were prepared by melting. The quartz ampules with their content were heated up to 1280 K, which exceeds by 20 K the melting point of the compound with the highest melting point in this system (CuInSe$_2$), and were maintained at
this temperature for 2 hours. The cooling was carried out with a velocity of 3-5 K/min. The isothermal annealing was at 683 K during 550 hours.

The phase relations in the CuSbSe$_2$-CuInSe$_2$ system were investigated by means of X-ray powder diffraction (DRON 3 diffractometer, monochromatic Cu K$_{\alpha}$-radiation, 1.5406 Å, step size 0.01° or 0.04°, counting time 10 s), optical microscopy (MIM 7 microscope), and scanning electron microscopy (Jeol electron microscope, equipped with an energy-dispersive X-ray detector, EDX). Microstructure was studied on the freshly-polished samples without additional etching.

RESULTS AND DISCUSSION

X-ray powder diffraction studies

The XRPD pattern of CuInSe$_2$ has in the range from 20 to 90 degrees the characteristic peaks (112), (103), (211), (105), (213), (204)/(220), (116), (312), (008), (400), (316), (332), (228), (424), (336), and (512), which correspond to the chalcopyrite-like tetragonal structure (SG: I4 \_2d) with the lattice constants 5.782 and 11.62 Å for \( a \) and \( c \), respectively (figure 1).

![Figure 1. XRPD patterns at room temperature for CuInSe$_2$ (1), CuSbSe$_2$ (0), and alloys of the (CuSbSe$_2$)$_{1-x}$(CuInSe$_2$)$_x$ system. The denotations of XRPD patterns for alloys correspond to their initial composition, expressed in mole fraction of CuInSe$_2$. The Bragg peaks of the phase with the chalcopyrite-like structure are denoted by a * and the Bragg peaks of the phase with the orthorhombic structure are denoted by a ○.](image-url)
CuSbSe$_2$ crystallizes in the orthorhombic structure (SG: Pnma) with the lattice constants 6.303, 3.976, and 15.008 Å for $a$, $b$, and $c$, respectively. The difference of the lattice constants with the values given in [14] may be explained by the difference in chemical compositions of the samples, which can vary inside the region of homogeneity of CuSbSe$_2$. The XRPD data show that all prepared alloys of the CuSbSe$_2$-CuInSe$_2$ system consist of two phases. From the XRPD results it can be concluded that the solubility of CuInSe$_2$ in CuSbSe$_2$ and CuSbSe$_2$ in CuInSe$_2$ does not exceed 0.05 mole fraction of the ternary compound.

**Microstructure studies**

The microstructure studies using optical microscopy and scanning electron microscopy confirmed the absence of the formation of complete solid solutions in the CuSbSe$_2$-CuInSe$_2$ system as they showed that all of the prepared alloys were biphasic (figure 2).

**Figure 2.** Microstructure of alloys of the (CuSbSe$_2$)$_{1-x}$(CuInSe$_2$)$_x$ system with $x = 0.15$ (a), 0.50 (b), 0.75 (c), and 0.95 (d) mole fraction of CuInSe$_2$

The primary crystals with the chalcopyrite-like structure, based on the compound with a higher melting point (CuInSe$_2$), crystallize in regular form. The regularity of crystallographic forms is detected as dendrites in figure 2a, b (grains of black color). When the content of CuInSe$_2$
increases these primary crystals are completely growing together and a phase based on CuSbSe$_2$
is detected as irregular inclusions (figure 2c, white color) or thin veinlets (figure 2d, white color).
Thus, two prevailing colors on the photographs of the microsection—black and white—indicate
the presence of two phases with different chemical compositions and crystal structures. Each
of these phases has an area of homogeneity, within the limits of which its chemical composition can vary. Because of such variation of chemical composition in addition to the black and white
colors one can also observe on the photographs their shades—several levels of dark to light grey.
The results of the determination of the chemical composition of these two phases are
presented in table I. The chemical composition for copper antimony diselenide CuSbSe$_2$ is
CuSb$_{0.94}$Se$_{1.99}$, which indicates a slight deficiency of antimony. This result is in accordance with
the previous results which establish that the homogeneity region of CuSbSe$_2$ is shifted toward the
Cu$_2$Se binary compound on the Cu$_2$Se-Sb$_2$Se$_3$ intersection and the solubility of Cu$_2$Se in
CuSbSe$_2$ is higher than the solubility of Sb$_2$Se$_3$ in CuSbSe$_2$ (0.0068 mole fraction versus 0.0020
mole fraction) [13]. The EDX results also confirmed a full interaction of all constituent
elements, as theoretical (initial) compositions of alloys agree well with the experimental total
compositions of alloys. For the alloy with the initial composition CuIn$_{0.50}$Sb$_{0.50}$Se$_2$ (an atomic
ratio In/Sb = 1) the atomic ratio In/Sb for experimental total composition of alloy is 0.60/0.59 =
1.02, and for the alloy with the initial composition CuIn$_{0.75}$Sb$_{0.25}$Se$_2$ (an atomic ratio In/Sb = 3)
the atomic ratio In/Sb for experimental total composition of alloy is 0.70/0.21 = 3.33.

Table I. Chemical composition of discovered phases for the (CuSbSe$_2$)$_{1-x}$(CuInSe$_2$)$_x$ alloys,
determined from Energy Dispersive X-ray analysis.

<table>
<thead>
<tr>
<th>Theoretical composition of alloy</th>
<th>Experimental total composition of alloy</th>
<th>Phase with the tetragonal structure</th>
<th>Phase with the orthorhombic structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSbSe$_2$</td>
<td>CuSb$<em>{0.94}$Se$</em>{1.99}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuIn$<em>{0.15}$Sb$</em>{0.85}$Se$_2$</td>
<td>CuIn$<em>{0.60}$Sb$</em>{0.50}$Se$_{1.87}$</td>
<td>CuIn$<em>{0.96}$Se$</em>{2.07}$</td>
<td>CuSb$<em>{0.85}$Se$</em>{1.69}$</td>
</tr>
<tr>
<td>CuIn$<em>{0.50}$Sb$</em>{0.50}$Se$_2$</td>
<td>CuIn$<em>{0.70}$Sb$</em>{0.21}$Se$_{2.34}$</td>
<td>CuIn$<em>{0.78}$Se$</em>{1.90}$</td>
<td>CuSb$<em>{0.84}$Se$</em>{1.69}$</td>
</tr>
<tr>
<td>CuIn$<em>{0.75}$Sb$</em>{0.25}$Se$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuIn$<em>{0.95}$Sb$</em>{0.05}$Se$_2$</td>
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</tbody>
</table>

Chemical compositions of the two phases detected on the polished sections correspond to
the chemical compositions of the phase with the tetragonal structure (average composition
CuIn$_{0.87}$Se$_{1.99}$) and the phase with the orthorhombic structure (average composition
CuSb$_{0.87}$Se$_{1.90}$). These phases contain only three chemical elements which indicate that the
solubility of antimony in CuInSe$_2$ and the solubility of indium in CuSbSe$_2$ do not exceed the
limits of determination of these elements by energy-dispersive X-ray analysis. It can be
concluded that the limits of solubility for CuSbSe$_2$ in CuInSe$_2$ and for CuInSe$_2$ in CuSbSe$_2$ do
not exceed 0.001 mole fraction. This result is in contrast to the limits of solubility in the CuInS$_2$-
CuSbS$_2$ system where the limits of solubility are 0.059 mole fraction for CuSbS$_2$ in CuInS$_2$ and
0.038 mole fraction for CuInS$_2$ in CuSbS$_2$.

CONCLUSIONS

The CuInSe$_2$ and CuSbSe$_2$ ternary compounds and alloys of the (CuSbSe$_2$)$_{1-x}$(CuInSe$_2$)$_x$
system with the mole fraction of CuInSe$_2$ (x) equal to 0.05, 0.15, 0.25, 0.375, 0.50, 0.625, 0.75,
0.85, and 0.95 were prepared and the phase relations in this system were investigated by X-ray powder diffraction, optical microscopy, and scanning electron microscopy. XRPD found that CuInSe$_2$ crystallizes in the chalcopyrite-like tetragonal structure (space group: I4\(\overline{2}\)d) with the lattice constants 5.782 and 11.62 Å for \(a\) and \(c\), respectively, and CuSbSe$_2$ crystallizes in the orthorhombic structure (space group: Pnma) with the lattice constants 6.303, 3.976, and 15.008 Å \(a\), \(b\), and \(c\), respectively. Chemical composition of copper antimony diselenide has a slight deficiency of antimony and corresponds to CuSb$_{0.94}$Se$_{1.99}$. This result can be explained by the shift of composition inside the homogeneity region of CuSbSe$_2$ toward Cu$_2$Se binary compound on the Cu$_2$Se-Sb$_2$Se$_3$ intersection. It was shown that the alloys of the CuSbSe$_2$-CuInSe$_2$ at room temperature are biphasic in the whole range of compositions, and the limits of solubility for CuSbSe$_2$ in CuInSe$_2$ and for CuInSe$_2$ in CuSbSe$_2$ do not exceed 0.001 mole fraction.

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