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## Phase Equilibrium of $\text{CuInSe}_2$ with Silicon, Germany, Tin and Lead Monoselenides

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**Abstract** The character of the interaction of  $\text{CuInSe}_2$  with monoselenides of silicon, germanium, tin, and lead was studied by the methods of differential thermal (DTA), X-ray phase (XRD), microstructural (MSA) analyzes, by measuring microhardness. The  $\text{CuInSe}_2$ -SiSe and  $\text{CuInSe}_2$ -GeSe systems are non-quasibinary and crystallization in them is completed by four-phase peritectic reactions of SiSe and GeSe formation. Phase diagrams of tin and lead systems are eutectic types with limited solubility. The eutectics of the  $\text{CuInSe}_2$ -SnSe system is crystallized at 720 °C and 82 mol. % SnSe, and of the  $\text{CuInSe}_2$ -PbSe system – at 735 °C and 72 mol. % SnSe.

**Keywords** systems, phase equilibrium, chalcopyrite phase, primary crystallization

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### Introduction

The chalcopyrite phase of the  $\text{CuInSe}_2$  compound is one of the promising materials for the solar photovoltaic converter [1-3]. Preparation of  $\text{CuInSe}_2$  film single crystals from a melt – solvent is one of the promising areas of research [4–7]. Direct growth of the chalcopyrite phase of  $\text{CuInSe}_2$  from a stoichiometric composition by methods of directed crystallization or zone melting will not succeed, due to the difference in the coefficients of thermal expansion of crystals, as well as, phase transition of sphalerite-chalcopyrite, where transformation of the crystal structure occurs, which leads to twinning of crystals, appearance of numerous defects and cracking [7].

More perfect crystals of the chalcopyrite phase of the  $\text{CuInSe}_2$  compound can be obtained by low-temperature methods, where crystal growth occurs as a result of cooling from solutions in melt. In the case of using a non-aqueous solvent, the growth occurs “from a solution in the melt”, where eutectic forming components are used as a solvent.

The method requires knowledge of the phase diagrams of the main substance – solvent system and crystallization is carried out from the zone of the liquidus curves of the system, where the main substance is crystallized primarily. In this case, it is the low-temperature modification of the  $\text{CuInSe}_2$  compound.

In the present work, the possibility of using monoselenides of the elements of the germanium and silicon subgroup as solvents for the primary crystallization of the low-temperature chalcopyrite phase of the  $\text{CuInSe}_2$  compound is clarified. For this purpose, the character of the interaction in the systems  $\text{CuInSe}_2$ -SiSe,  $\text{CuInSe}_2$ -GeSe,  $\text{CuInSe}_2$ -SnSe and  $\text{CuInSe}_2$ -PbSe is studied.

### Experiment

The necessary samples for the study were prepared by fusion of highly pure elements (Copper-electrolytic grade MO, Indium grade In-000, Silicon, Germanium, Tin and Lead with an impurity content of less than 10-3%, Selenium



HP 19-4). Fusion was carried out in evacuated ( $\sim 0.1$  Pa) quartz ampoules with mechanical vibration in the liquid state. After synthesis, the alloys were heated at  $600^\circ\text{C}$  during 200 hours. Achievement of equilibrium in the alloys was controlled by periodic testing of their microstructure.

Thermograms were recorded using a chromel-alumel thermocouple on a two-coordinate potentiometer (brand N307/1). Calcined alumina was used as a reference material. The values of the obtained thermal effects are reflected in the phase diagrams (Fig. 1, 2).

X-ray diffraction patterns of some alloys of the system were recorded using a D2 PHASER diffractometer using  $\text{CuK}\alpha$  radiation with a nickel filter. The results for the  $\text{CuInSe}_2$ -PbSe system are shown in Fig. 3.

The microstructures of polished samples were examined on a METAM-P1 metallographic microscope, and microhardness measurements were carried out on a PMT-3 microhardness meter under a load of 20g.

Phase diagrams were constructed on the basis of the data of DTA, X-ray, MSA and microhardness measurements.

## Results and Conclusions

### Phase diagram of the $\text{CuInSe}_2$ -SiSe system

The results of previous works on hypothetical phase diagrams are summarized in [8], where the existence of two chemical compounds,  $\text{SiSe}_2$  and  $\text{SiSe}$ , is determined. The first compound melts congruently at  $1243 \pm 5$  K, and the  $\text{SiSe}$  compound melts incongruently by the reaction:  $\text{L} + \text{Si} \leftrightarrow \text{SiSe}$  at about 1573 K [9]. It is formed by the interaction of elementary Si and Se, taken in stoichiometric proportions at 1023K. The  $\text{SiSe}$  compound is gradually hydrolyzed by air moisture with the release of hydrogen selenide.

To prepare the samples, calculated amount of the ingredients  $\text{CuInSe}_2$ , Si, and Se is gradually heated to  $800^\circ\text{C}$ ; after an hour of exposure, the temperature was raised to  $1100^\circ\text{C}$ . At this temperature, the melt was in a liquid state and mixed several times. During cooling of melts rich in silicon, cracking of quartz ampoules is possible.

Thermal analysis was carried out up to  $1100^\circ\text{C}$  and a phase diagram was constructed (Fig. 1a). It is not quasi-binary system. Crystallization is completed by the four-phase peritectic reaction  $\text{L} + \text{Si} \leftrightarrow \alpha\text{-CuInSe}_2 + \text{SiSe}$  at  $710^\circ\text{C}$  temperature and 56 mol.% SiSe. Subsolidus has two phases:  $\alpha\text{-CuInSe}_2$  and  $\text{SiSe}$ . There is no solubility based on the starting compounds [10, 11].

The  $\alpha \leftrightarrow \beta$  transition of the  $\text{CuInSe}_2$  compound occurs reversibly at  $810^\circ\text{C}$  and the isothermal line of this phase transition crosses the liquidus curve at a composition of 41 mol.% SiSe. The chalcopyrite phase of the  $\text{CuInSe}_2$  compound primarily crystallizes from the melt. From the metatatic point to 54 mol% of SiSe.

**Phase diagram of the  $\text{CuInSe}_2$  – GeSe system** [11–13]. The GeSe compound is formed by the peritectic reaction  $\text{L} + \text{Ge} \leftrightarrow \text{GeSe}$  at  $675^\circ\text{C}$  and has a polymorphic transition at  $666^\circ\text{C}$ .

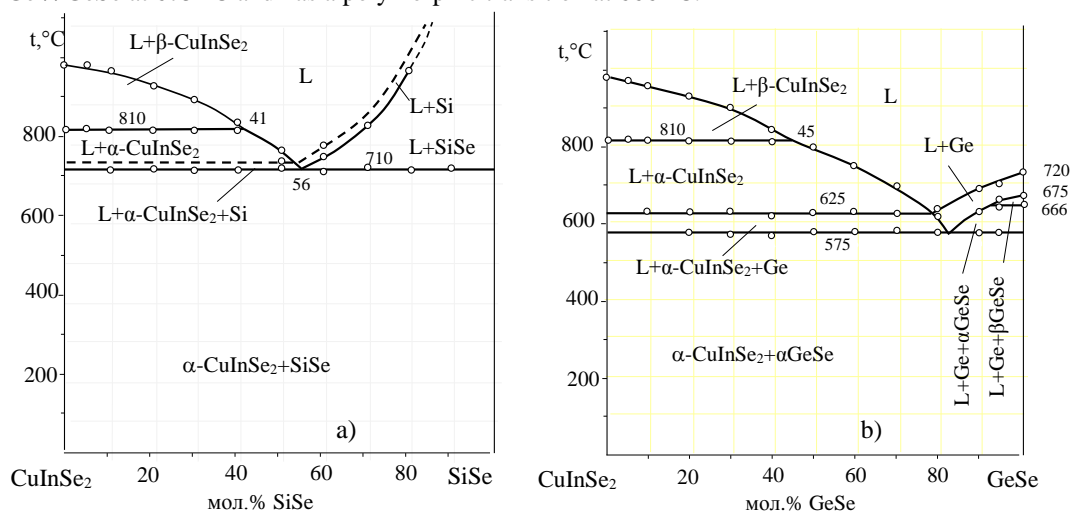


Figure 1: Phase diagrams of the  $\text{CuInSe}_2$ -SiSe (a) and  $\text{CuInSe}_2$ -GeSe (b) systems



The phase diagram of the  $\text{CuInSe}_2\text{-GeSe}$  system, constructed by the results of physicochemical analyzes, is presented in Figure 1b. Four isothermal processes were detected in the system:

- at 810°C - polymorphic transition of the  $\text{CuInSe}_2$  compound;
- at 666°C - polymorphic transition of the  $\text{GeSe}$  compound
- at 625°C - secondary release of germanium from the melt;
- at 575°C - the peritectic process of formation of  $\text{GeSe}$  in the melt.

The isothermal line at 810 °C crosses the liquidus curve at 44 mol.%  $\text{GeSe}$  and up to 78 mol.%  $\text{GeSe}$  and primary isolation of the chalcopyrite phase of the  $\text{CuInSe}_2$  compound occurs.

Crystallization in the system is completed by the peritectic reaction:



Using X-ray analysis, the two-phase nature of the alloys in the subsolidus part of the system was determined. The X-ray diffraction patterns contain only reflections of  $\alpha\text{-CuInSe}_2$  and  $\alpha\text{-GeSe}$  compounds. Solubility based on the chalcopyrite phase is virtually non-existent.

**The phase diagram of the  $\text{CuInSe}_2\text{-SnSe}$  system**, shown in Fig. 2a, refers to eutectic diagrams with monotectics and limited solubility from the side of  $\text{CuInSe}_2$  [14, 15]. The eutectic of the system is crystallized at 715 °C and 82 mol. %  $\text{SnSe}$ . The monotectic process occurs at 730 °C, and the region of delamination in liquid melts covers the concentration range from 63 to 81 mol. %  $\text{SnSe}$ . Another isothermal line at 800 °C is linked by the sphalerite-chalcopyrite polymorphic transition in alloys. At this temperature, the region of solid solutions reaches up to 5 mol. %  $\text{SnSe}$  and narrows with decreasing temperature to 2 mol. %  $\text{SnSe}$  (at room temperature).

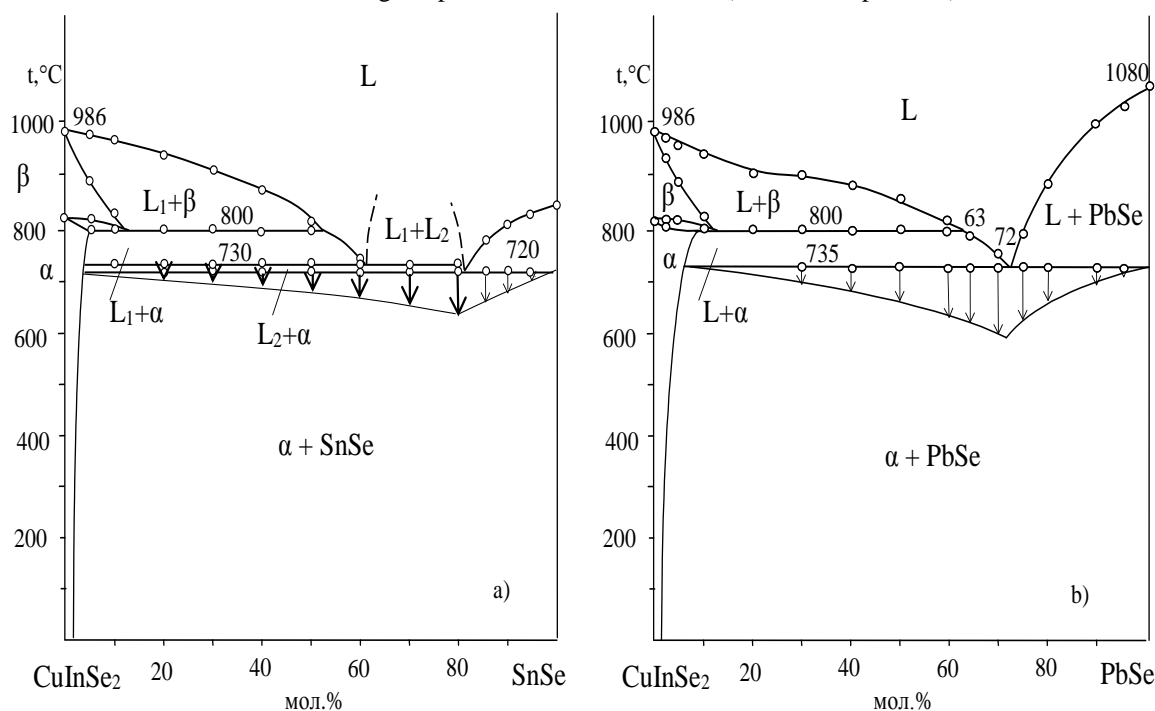


Figure 2: Phase diagrams of the  $\text{CuInSe}_2\text{-SnSe}$  (a) [15] and  $\text{CuInSe}_2\text{-PbSe}$  (b) systems [17]

Thus, the chalcopyrite phase of the  $\text{CuInSe}_2$  compound is crystallized directly from the molten liquid in the  $\text{CuInSe}_2\text{-SnSe}$  system in the concentration range of 52-63 mol. %  $\text{SnSe}$ .

**Phase diagram of the  $\text{CuInSe}_2\text{-PbSe}$  system.**  $\text{PbSe}$  is the only one compound in the  $\text{Pb - Se}$  system and it melts congruently at 1080°C. The  $\text{CuInSe}_2\text{-PbSe}$  is quasibinary system and its phase diagram is one of the eutectic types with limited solubility on the  $\text{CuInSe}_2$  side (Fig. 2b) [16, 17]. The boundary of solid solutions extends up to 2 mol%  $\text{PbSe}$  at room temperature. The remaining alloys are two-phases (Fig. 3).



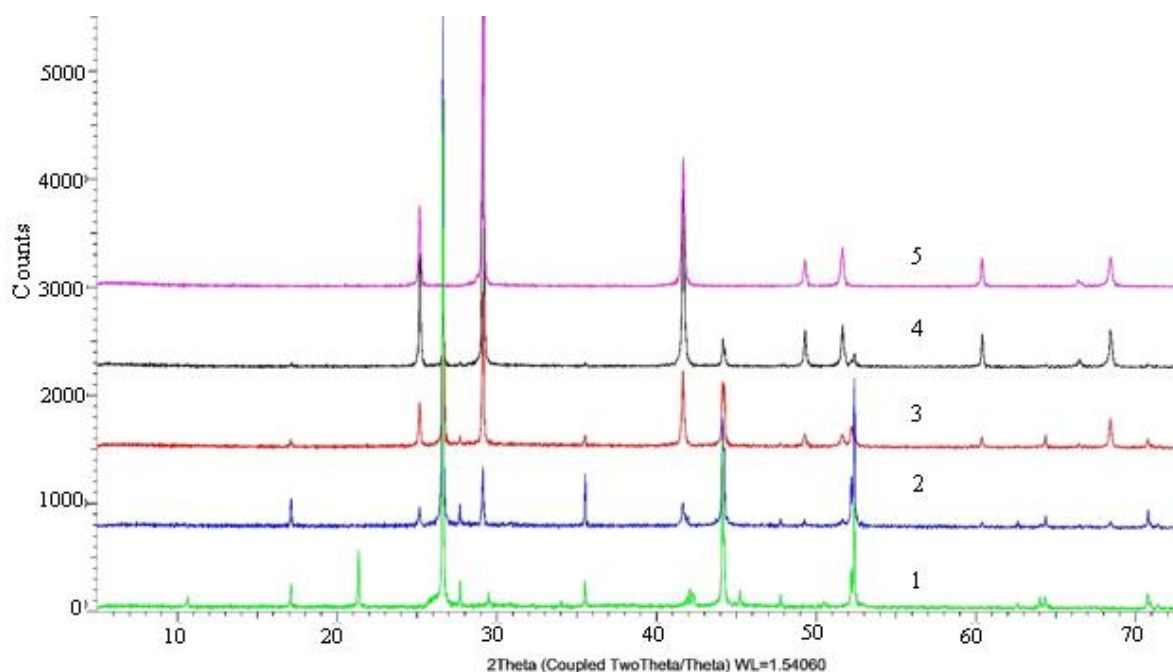


Figure 3: Diffraction patterns of some samples of the  $\text{CuInSe}_2$  -  $\text{PbSe}$  system. Compositions: 1-  $\text{CuInSe}_2$ ; 2-10 mol%  $\text{PbSe}$ ; 3-50 mol%  $\text{PbSe}$ ; 4-90; 5-  $\text{PbSe}$

Only X-ray reflections of the  $\alpha$  phase (solid solution based on  $\alpha$ - $\text{CuInSe}_2$ ) and lead selenide are observed in the diffraction pattern. In the region of  $\alpha$  solid solutions, the maxima of X-ray reflexes slightly shifted toward large angles. The polymorphic  $\text{CuInSe}_2$  transition in alloys occurs at 800 °C.  $\alpha$ - $\text{CuInSe}_2$  is crystallizes primarily in the concentration range of 63–72 mol%  $\text{PbSe}$ .

The eutectic of the system is crystallized at 735 °C and 72 mol.%  $\text{PbSe}$ . Here, the eutectic has a striped structure.

### Conclusion

Phase equilibria in  $\text{CuInSe}_2$ -MeSe systems (where Me-Si, Ge, Sn, Pb) were studied by using the methods of physicochemical analysis. It was established that the  $\text{CuInSe}_2$ -SnSe and  $\text{CuInSe}_2$ -PbSe systems are eutectic types with limited solubility on the basis of the chalcoprite phase. The  $\text{CuInSe}_2$ -SiSe and  $\text{CuInSe}_2$ -GeSe systems are non-quasibinary. In all studied systems, concentration regions were determined, where crystallization of the low-temperature chalcoprite phase occurs directly from liquid melts.

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