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PHASE EQUILIBRIA IN THE $CuInSe_2$-Ge-Se QUASİTERNARY SYSTEM

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Abstract: *Phase equilibria in the $CuInSe_2$-Ge-Se ternary system were studied by methods of differential thermal analysis (DTA), X-ray phase (XRD), microstructural (MSA) analyzes and measurement of microhardness. Results of these studies were summarized and presented in the paper. Phase diagrams of $CuInSe_2$-Ge, $CuInSe_2$-GeSe, $CuInGeSe_4$ - Ge, $CuInGeSe_4$ – GeSe, $CuInGeSe_4$ -Se and liquidus surface projections of quasi-ternary system established and monovariant curves, regions of phase delamination in the liquid state, coordinates of monotectic, metathetic, peritectic and eutectic processes determined. Also, a region of primary crystallization of a low-temperature polymorphic form (phase with a chalcopyrite structure) of the $CuInSe_2$ compound in the presence of germanium chalcogenides specified.*

Keywords: *system, chalcopyrite phase, phase equilibria, liquidus surface projection, chalcopyrite phase, phase transition*

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Introduction

The low-temperature chalcopyrite phase of the $CuInSe_2$ compound is of interest as a solar energy converter [1-3]. However, its conversion coefficient strongly depends on imperfections of the crystal structure which are formed mainly during the polymorphic transition of sphalerite ↔ chalcopyrite. Therefore, to reduce these imperfections, crystallization is carried out by flux method [4-5].

Earlier, we presented results of the study of phase equilibria in the $CuInSe_2$-Sn-Se and $CuInSe_2$-Pb-Se systems where regions of primary crystallization of α-$CuInSe_2$ directly from the liquid melt were determined [6, 7].

In the present work, the possibility of using germanium and its selenides as solvents for the primary crystallization of the chalcopyrite phase of the $CuInSe_2$ compound was clarified. For this purpose, the pattern of interaction of $CuInSe_2$-Ge-Se system components was determined, especially in areas where the chalcopyrite phase of the $CuInSe_2$ compound was directly crystallized from the liquid melt.

Experimental part

The initial samples for the study were synthesized by fusion from calculated amounts of highly pure elements (copper - grade M0, indium grade In-000, germanium with a resistivity of 40 Ohm cm, selenium grade OSCH 19-4) in evacuated (~ 0.1 Pa) and sealed quartz ampoules at 1100^0 C for 6 hours. Then the furnace was cooled to 600^0 C and stored for 200 hours.

The resulting ingots were equilibrium polycrystals and characterized by differential thermal analysis (DTA) and X-ray diffraction (XRD).

During DTA, the phase transition temperatures were determined using a chromel/alumel thermocouple with a heating and cooling rate of 10 K/min on a two-coordinate potentiometer N307/1. Calcined aluminum oxide served as a reference.

X-ray powder diffraction patterns were recorded with Bruker D8 diffractometer using CuKα radiation with a nickel filter.

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

Results and discussion

The nature of physicochemical interaction of some sections of the ternary system $CuInSe_2$-Ge-Se is presented below. Also, projections of the liquidus surface were constructed.

The $CuInSe_2$-Ge section is quasibinary. Phase diagram of this section is eutectic, there is a region of immiscibility on the side of germanium (Fig. 1a). The eutectic crystallizes at 50 mol.% Ge and 7900C. The monotectic process occurrs at 8500C in the area of 67-87 mol.% Ge.

The $CuInSe_2$-GeSe section is non-quasi-binary and quasi-stable simultaneously, since just two phases α-$CuInSe_2$ and α-GeSe are determined in the sub-solidus of the system (Fig. 1b).

Under the influence of germanium mono-selenide, the temperature of the polymorphic transition of the $CuInSe_2$ compound does not change, and the isothermal line of this transition, determined at 810^0C, crosses the liquidus at 44 mol.% GeSe. Primary crystallization of the chalcopyrite phase (α-$CuInSe_2$) occurs directly from the liquid melt in the concentration region 44–78 mol% of GeSe.

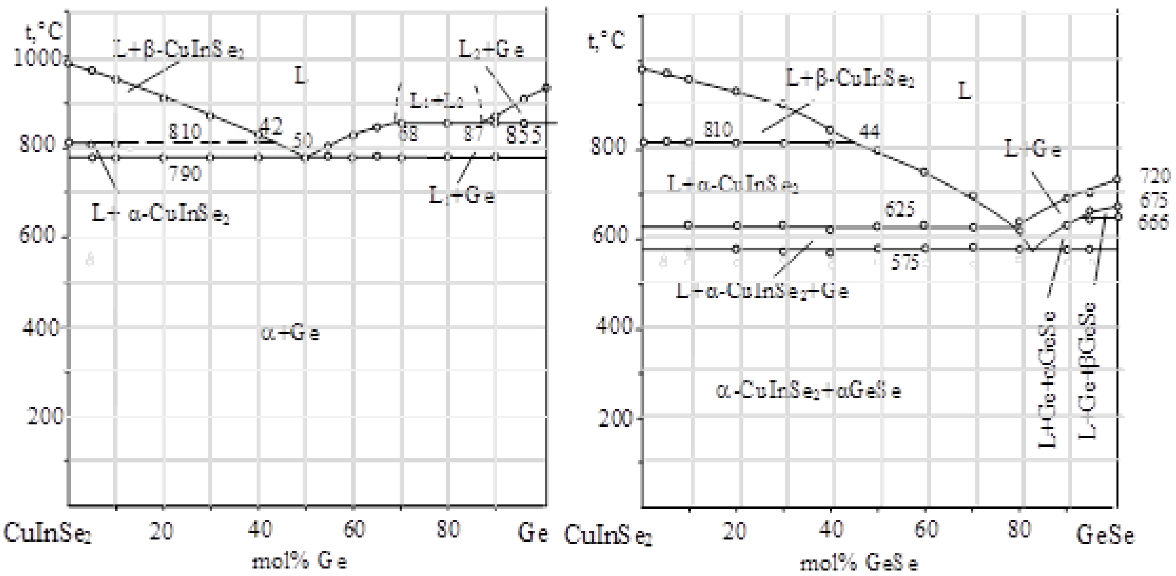

Fig. 1. Phase diagrams of the $CuInSe_2$-Ge (a) and $CuInSe_2$-GeSe (b) systems.

As, it is known, GeSe is formed by peritectic between the liquid and germanium. In the section, before intersection of liquidus (α-$CuInSe_2$) curves, the temperature of primary crystallization of germanium decreases from 720 to 625^0C. Crystallization in the system is over through four-phase peritectic reaction:

$$L + Ge \leftrightarrow \alpha\text{-}GeSe \quad \text{at } 575^0C$$

Solubility based on the starting components is practically absent.

The $CuInGeSe_4$-Ge section is non-quasibinary. According to [8, 9], the $CuInGeSe_4$ compound is formed by the peritectic reaction in the quasibinary $CuInSe_2$-$GeSe_2$ system at 712^0C.

The liquidus of the $CuInGeSe_4$-Ge system consists of two primary crystallization curves of α-$CuInSe_2$ and germanium, which intersect at 40 at% Ge and 640^0C (Fig.2a).

The $CuInGeSe_4$-GeSe section is non-quasi-binary. The liquidus of the system consists of two curves of primary crystallization of α-$CuInSe_2$ and germanium that intersect at 40 mol% GeSe and 660^{0}C (Fig. 2b).

Crystallization in the system is completed by a four-phase peritectic reaction:

$$L + \alpha\text{-}CuInSe_2 \leftrightarrow CuInGeSe_4 + \alpha\text{-}GeSe \quad \text{at } 575^0C$$

Solubility based on the starting components is practically absent.

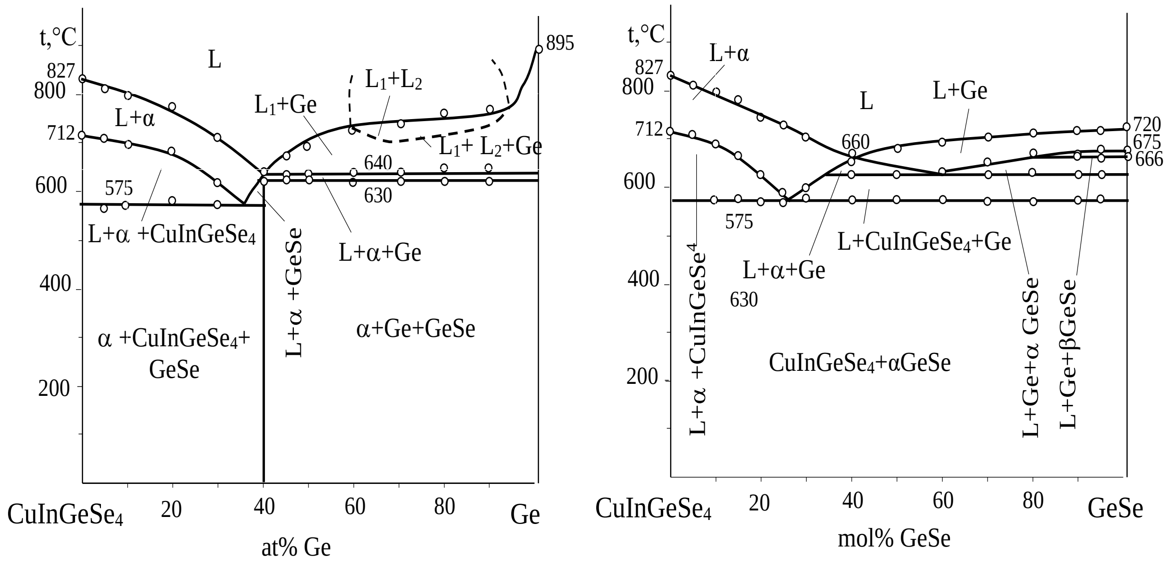

Fig. 2. Phase diagrams of the $CuInGeSe_4$ - Ge (a) and $CuInGeSe_4$ - GeSe (b) systems.

The $CuInGeSe_4$-Se section is quasi-stable and participates in the incongruent triangulation of the $CuInSe_2$-Ge-Se ternary system. The liquidus of the system mainly consists of the curve of the primary crystallization of the α-phase (the low-temperature polymorphic form of $CuInSe_2$) (Fig. 3). Crystallization in the system is completed at a temperature of ternary peritectic, 215^{0}C. There is no solubility based on the starting components.

The microhardness of the $CuInGeSe_4$ phase is determined at 300 MPa, and the microhardness of the selenium phase is 450 MPa.

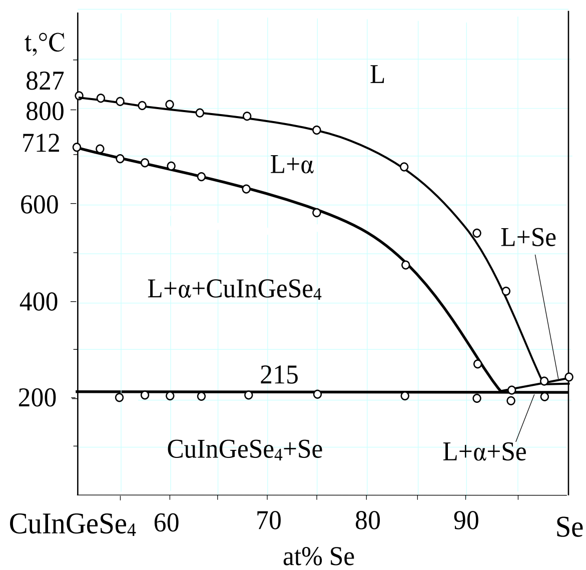

Fig. 3. Phase diagram of the $CuInGeSe_4$ - Se system

The projection of the liquidus surface of the $CuInSe_2$-Ge-Se system (Fig. 4) is constructed on the data of phase diagrams of the above-mentioned sections of the quasi binary systems $CuInSe_2$-$GeSe_2$[8], $CuInSe_2$-Se [10] and Ge-Se [6]. Here, the quasibinary section $CuInSe_2$ – $GeSe_2$ is a diagonal section and divides the quasi ternary system into two subsystems: $CuInSe_2$ – $GeSe_2$ – Se and $CuInSe_2$ – $GeSe_2$ – Ge.

In the first subsystem, two triple peritectic and one eutectic process were found:

{P_1}	L + Ge ↔ $CuInGeSe_4$ + GeSe	at 575^0C
{P_2}	L + $CuInSe_2$ ↔ $CuInGeSe_4$ + Ge	at 630^0C
{E_1}	L ↔ $CuInGeSe_4$ + GeSe + $GeSe_2$	at 560^0C

As known, metathetic processes in the $CuInSe_2$-Se and Ge-Se systems occur with the participation of germanium and the delamination regions are closer to germanium. In the quasi-ternary subsystem, these immiscible regions merge with each other and form one common immiscible region in the liquid state.

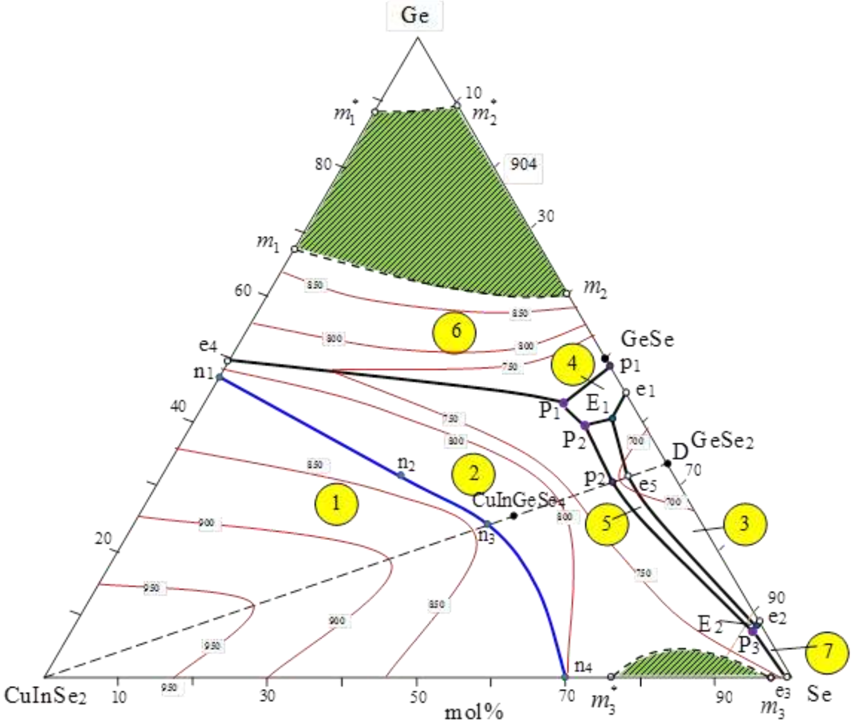

Fig. 4. Projection diagram of the liquidus surface of the $CuInSe_2$-Ge-Se system. Primary crystallization field: 1-β-$CuInSe_2$, 2-α-$CuInSe_2$, 3-$GeSe_2$, 4-, 5-$CuInGeSe_4$, 6-Ge, 7-Se

In the first subsystem, β-$CuInSe_2$, α-CuInSe, $GeSe_2$, GeSe and germanium phases are crystallized primarily. A part of the primary crystallization of germanium occurs under monotectic line.

In the second subsystem, the phases β-$CuInSe_2$, α-$CuInSe_2$, $GeSe_2$ and selenium are primarily crystallized. A part of the primary crystallization of α-$CuInSe_2$ occurrs under delamination. Here crystallization is over at 200^0 C in a triple eutectic, the composition of which is designated as E_2. Prior to this, a four-phase peritectic process of separation of the $CuInGeSe_4$ compound takes place along the isothermal plane at 215^0C.

Conclusions

Thus, 7 fields of primary crystallization of phases are established in the quasi-ternary $CuInSe_2$ – Ge – Se system and phase equilibria were studied. The transition boundary of the primary crystallization fields α-$CuInSe_2$ and β-$CuInSe_2$ was determined, it is indicated in Fig. 4 by blue line ($n_1n_2n_3n_4$).

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$CuInSe_2$-Ge-Se KVAZİÜÇLÜ SİSTEMİNDƏ FAZA TARAZLIĞI

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Differensial-termiki (DTA), rentgen-faza (RFA), mikroquruluş (MQA) və mikrobərkliyin ölçülməsi üsulları ilə $CuInSe_2$-Ge-Se üçlü sisteminin bütün qatılıq sahələrində faza tarazlığı öyrənilmişdir və nəticələr ümumiləşdirilib və bu məqalədə verilir. Kvaziüçlü sistemin $CuInSe_2$-Ge, $CuInSe_2$-GeSe, $CuInGeSe_4$ - Ge, $CuInGeSe_4$ – GeSe, $CuInGeSe_4$ -Se kəsiklərinin faza diaqramları və özünün likvidus səthinin ortoqonal proyeksiyası qurulmuşdur. Sistem daxilində maye fazada təbəqələşmə sahəsi, monovariant əyrilər, monotektik, metatektik, peritektik və evtektik proseslərin koordinatları təyin edilmişdir. $CuInSe_2$ birləşməsinin aşağı temperaturlu polimorf formasının (xalkopirit quruluşlu fazanın) ilkin kristallaşma sahələrinə germanium xalkogenidlərinin təsiri dəqiqləşdirilmişdir.

Açar sözlər: *sistem, faza tarazılığı, likvidus səthinin proyeksiyası, xalkopirit fazası, faza keçidi*

ФАЗОВЫЕ РАВНОВЕСИЯ В КВАЗИТРОЙНОЙ СИСТЕМЕ $CuInSe_2$-Ge-Se

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Методами дифференциально-термического (ДТА), рентгенофазового (РФА), микроструктурного (МСА) и измерением микротвердости исследованы фазовые равновесия в тройной системе CuInSe2-Ge-Se во всей концентрационной области. Результаты исследований обобщены и представлены в настоящей статье. Установлены фазовые диаграммы систем $CuInSe_2$- Ge, $CuInSe_2$-GeSe, $CuInGeSe_4$ - Ge, $CuInGeSe_4$ – GeSe, $CuInGeSe_4$ - Se, а также диаграммы проекции поверхности ликвидуса квазитройной системы. Определены моновариантные кривые, области расслаивания фаз в жидком состоянии, координаты монотектических, метатектических, перитектических и эвтектических процессов. Уточнены область первичной кристаллизации низкотемпературной полиморфной формы (фазы со структурой халькопирита) соединения $CuInSe_2$ в присутствие халькогенидов германия.

Ключевые слова: *система, фазовые равновесия, проекция поверхности ликвидуса, халькопиритная фаза, фазовый переход.*