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Quasi-Ternary System Cu_2Se-$GeSe_2$-As_2Se_3

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Abstract Direct single-temperature method has been employed to synthesize 137 samples of the Cu_2Se-$GeSe_2$-As_2Se_3 system. The samples have been investigated by x-ray diffraction and differential thermal analysis. The isothermal section at 513 K (240 °C), two phase diagrams $GeSe_2$-As_2Se_3 and Cu_2GeSe_3-As_2Se_3, four vertical sections Cu_2GeSe_3-$CuAsSe_2$, Cu_8GeSe_6-$CuAsSe_2$, Cu_8GeSe_6-As_2Se_3, *A*-*B* (*A* = 85 mol.% $GeSe_2$-15 mol.% Cu_2Se; *B* = 85 mol.% As_2Se_3-15 mol.% Cu_2Se), and the liquidus surface projection onto the concentration triangle have been constructed. The existence of the ternary compounds Cu_2GeSe_3, Cu_8GeSe_6 and $CuAsSe_2$ have been confirmed. The fields of the primary crystallization of phases, character, temperatures and coordinates of nonvariant points have been determined.

Keywords isothermal section · liquidus surface projection · phase diagram · thermal analysis · x-ray powder diffraction

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1 Introduction

The binary compounds Cu_2Se, $GeSe_2$, As_2Se_3 melt congruently at 1421 K (1148 °C), 1013 K (740 °C), and 648 K (375 °C),[1] respectively, possess insignificant homogeneity regions and may serve as components of the quasi-ternary system Cu_2Se-$GeSe_2$-As_2Se_3. The study of this quasi-ternary system is of current interest because it is formed by binary compounds with important semiconducting properties.[2,3]

Phase equilibria in the quasi-binary system Cu_2Se-$GeSe_2$ were studied in Ref 4-7. Two ternary compounds were found in the system, Cu_2GeSe_3 and Cu_8GeSe_6.[4-7] Cu_2GeSe_3 melts congruently at 1053 K (780 °C), and Cu_8GeSe_6 is formed in the peritectic reaction at 1083 K (810 °C) and has two polymorphous transformations at 983 K (710 °C) and 333 K (60 °C).[7] The interactions of Cu_8GeSe_6 and Cu_2GeSe_3, Cu_2GeSe_3 and $GeSe_2$ are eutectic. The eutectic points have the following coordinates: e_1-38 mol.% $GeSe_2$ and 1033 K (760 °C); e_2-83 mol.% $GeSe_2$ and 960 K (687 °C). The Cu_2GeSe_3 compound crystallizes in space group *Imm2*, *a* = 1.1860(3) nm, *b* = 0.3960(1) nm, *c* = 0.5485(2) nm;[8] Cu_8GeSe_6 in space group $P6_3cm$, *a* = 1.2648(5) nm, *c* = 1.176(4) nm.[9]

The Cu_2Se-As_2Se_3 phase diagram was described in Ref 10-13. The system features one ternary compound $CuAsSe_2$ which melts incongruently at 725 K[10] and crystallizes in space group *R3* ($Cu_7As_6Se_{13}$ structure type) with the cell parameters *a* = 1.4025(3) nm, *c* = 0.961(3) nm.[14]

The $GeSe_2$-As_2Se_3 system is a section of the ternary system Ge-As-Se that was studied in terms of its glass-forming ability.[15-17] According to these studies, no intermediate phases form in the $GeSe_2$-As_2Se_3 system. No phase diagram of this system has been reported in the literature.

2 Experimental Methods

Phase equilibria in the quasi-ternary system Cu_2Se-$GeSe_2$-As_2Se_3 were studied on 137 samples. The alloys were synthesized by direct single-temperature method from high-purity elements (Cu 99.99, Ge 99.99, Se 99.9997, As 99.9999 wt.%) in evacuated to the residual pressure 0.133 Pa and sealed quartz containers. The synthesis was performed in a shaft-type furnace with temperature control with an accuracy of ± 5 K (± 5 °C). The maximum synthesis temperature was 1453 K (1180 °C), the heating and cooling rate was 10 K/h (10 °C/h). Homogenizing annealing at 513 K (240 °C) was held for 600 h, after which the samples were quenched into 25% aqueous NaCl solution.

Obtained samples were investigated by x-ray diffraction (XRD) method (DRON 4-13 diffractometer, CuK_α radiation, $10° < 2\theta < 80°$, 0.05° scan step, 1 s exposure in each point) and differential thermal analysis (DTA) ("Thermodent H307/1" furnace with a PDA-1 XY-recorder, Pt/Pt-Rh thermocouple). The two-phase or three-phase composition of the samples was also checked by the microstructural analysis (MSA), which was performed on a PMT-3M microhardness tester.

3 Results and Discussion

3.1 The Quasi-Binary System $GeSe_2$-As_2Se_3

Phase diagram of the $GeSe_2$-As_2Se_3 system was investigated by DTA and XRD methods (Fig. 1). The liquidus consists of the curves of the primary crystallization of α-solid solutions of $GeSe_2$ and β-solid solutions of As_2Se_3, which at 513 K (240 °C) extend to less than 4 mol.%. The system solidus is the eutectic horizontal at 618 K (345 °C). The eutectic point was determined by the Tamman triangle according to the literature[18] as 20 mol.% $GeSe_2$, 80 mol.% As_2Se_3. The alloys below the eutectic horizontal are two-phase.

3.2 The Quasi-Binary System Cu_2GeSe_3-As_2Se_3

The phase diagram of the Cu_2GeSe_3-As_2Se_3 system was constructed from XRD and DTA results (Fig. 2). The system liquidus consists of the curves of the primary crystallization of η-solid solutions of Cu_2GeSe_3 and β-solid solutions of As_2Se_3. Nonvariant eutectic process L ↔ η + β takes place at 633 K (360 °C). The eutectic point e_4

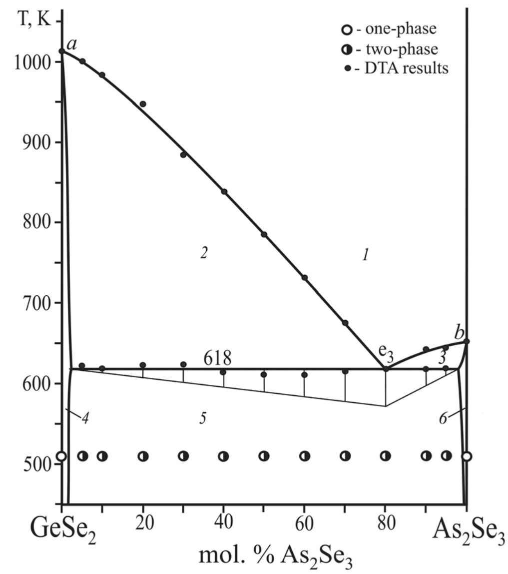

Fig. 1 Phase diagram of the $GeSe_2$-As_2Se_3 system: 1-L, 2-L + α, 3-L + β, 4-α, 5-α + β, 6-β (where α-solid solutions of $GeSe_2$, β-solid solutions of As_2Se_3)

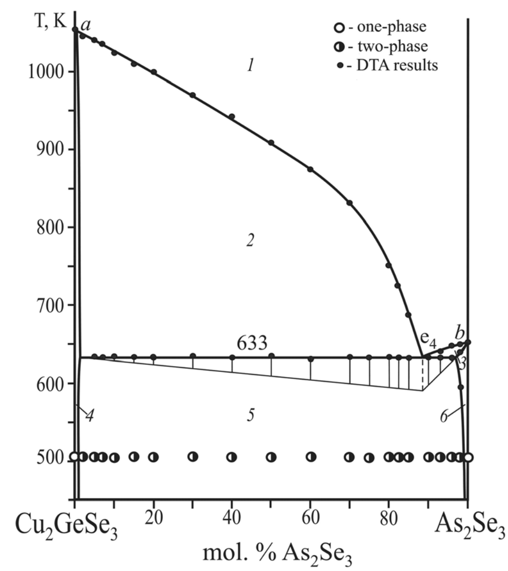

Fig. 2 Phase diagram of the Cu_2GeSe_3-As_2Se_3 system: 1-L, 2-L + η, 3-L + β, 4-η, 5-η + β, 6-β (where β-solid solutions of As_2Se_3, η-solid solutions of Cu_2GeSe_3)

was determined by the Tamman triangle as the composition of 11.7 mol.% Cu_2GeSe_3, 88.3 mol.% As_2Se_3. The alloys below the eutectic horizontal are two-phase, β-solid solutions of As_2Se_3 and η-solid solutions of Cu_2GeSe_3. The solid solubility at 513 K (240 °C) is less than 2 mol.% Cu_2GeSe_3 and 2 mol.% As_2Se_3, respectively.

3.3 The Vertical Section Cu_2GeSe_3-$CuAsSe_2$

The Cu_2GeSe_3-$CuAsSe_2$ section was investigated by DTA and XRD methods (Fig. 3). The section liquidus is represented by the curves of the primary crystallization: *ab* of η-solid solutions of Cu_2GeSe_3, *bc* of LTM-Cu_8GeSe_6, *cd* of γ-solid solutions of Cu_2Se. The section crosses the plane of the nonvariant peritectic process L_{U1} + γ ↔ LTM-Cu_8GeSe_6 + δ at 700 K (427 °C) (δ—solid solutions of $CuAsSe_2$), where the volumes of monovariant peritectic processes L + γ ↔ LTM-Cu_8GeSe_6 and L + γ ↔ δ converge. The plane of the nonvariant peritectic process L_{U2} + LTM-Cu_8GeSe_6 ↔ η + δ lies at 650 K (377 °C) and the volumes of monovariant eutectic processes L ↔ η + LTM-Cu_8GeSe_6 and L ↔ LTM-Cu_8GeSe_6 + δ converge to this plane. The nonvariant peritectic process at 650 K (377 °C) ends with the exhaustion of both L and the crystals of LTM-Cu_8GeSe_6, since this section is the connecting line of the plane of this peritectic process. Therefore, the section alloys below 650 K (377 °C) are two-phase as confirmed by XRD data (Fig. 3).

3.4 The Vertical Section Cu_8GeSe_6-$CuAsSe_2$

The Cu_8GeSe_6-$CuAsSe_2$ section was investigated from DTA and XRD results (Fig. 4). Liquidus of the section is the curve of primary crystallization of γ-solid solutions of Cu_2Se. The section then crosses the plane of the nonvariant process HTM-Cu_8GeSe_6 ↔ LTM-Cu_8GeSe_6 + γ + L_{U3} at 970 K (697 °C) which is due to the polymorphous transition of Cu_8GeSe_6 in the Cu_2Se-$GeSe_2$ system. The section crosses the plane of the nonvariant peritectic process L_{U1} + γ ↔ LTM-Cu_8GeSe_6 + δ at 700 K (427 °C). The process in the alloys of this section at this temperature ends with the exhaustion of both liquid and the crystals of γ-solid solutions of Cu_2Se because the section coincides with the connecting diagonal of the plane of the nonvariant peritectic process. Therefore, the alloys below 700 K (427 °C) are two-phase, LTM-Cu_8GeSe_6 and δ, which is confirmed by XRD results (Fig. 4).

3.5 The Vertical Section Cu_8GeSe_6-As_2Se_3

The Cu_8GeSe_6-As_2Se_3 section was investigated by DTA and XRD methods (Fig. 5). The section liquidus consists of the curves *ab* (of the primary crystallization of γ-solid solutions of Cu_2Se), *bc* LTM-Cu_8GeSe_6), *cd* (δ-solid solutions of $CuAsSe_2$), and *df* (β-solid solutions of As_2Se_3). The nonvariant process HTM-Cu_8GeSe_6 ↔ LTM-Cu_8GeSe_6 + γ + L_{U3} at 970 K (697 °C) is caused by the polymorphous transition of Cu_8GeSe_6 at 983 K (710 °C) in the Cu_2Se-$GeSe_2$ system. The section then crosses another plane of the nonvariant peritectic process L_{U2} + LTM-Cu_8GeSe_6 ↔ η + δ at 650 K (377 °C). The volume of the monovariant eutectic process L ↔ δ + LTM-Cu_8GeSe_6

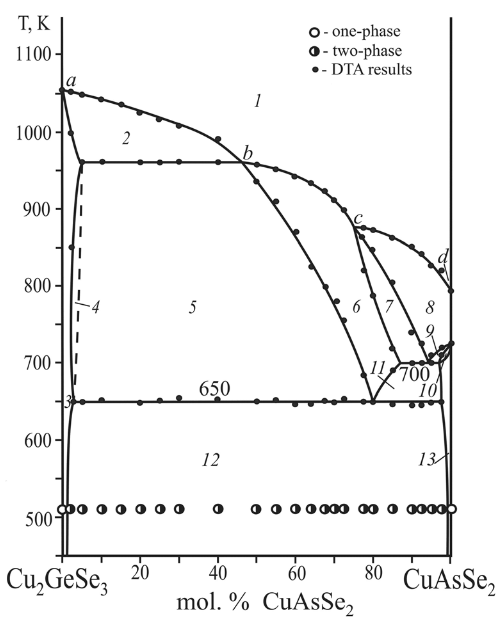

Fig. 3 The vertical section Cu_2GeSe_3-$CuAsSe_2$: 1-L, 2-L + η, 3-η, 4-η + LTM-Cu_8GeSe_6, 5-L + η + LTM-Cu_8GeSe_6, 6-L + LTM-Cu_8GeSe_6, 7-L + LTM-Cu_8GeSe_6 + γ, 8-L + γ, 9-L + γ + δ, 10-δ + γ, 11-L + LTM-Cu_8GeSe_6 + δ, 12-η + δ, 13-δ (where γ-solid solutions of Cu_2Se, δ-solid solutions of $CuAsSe_2$, η-solid solutions of Cu_2GeSe_3)

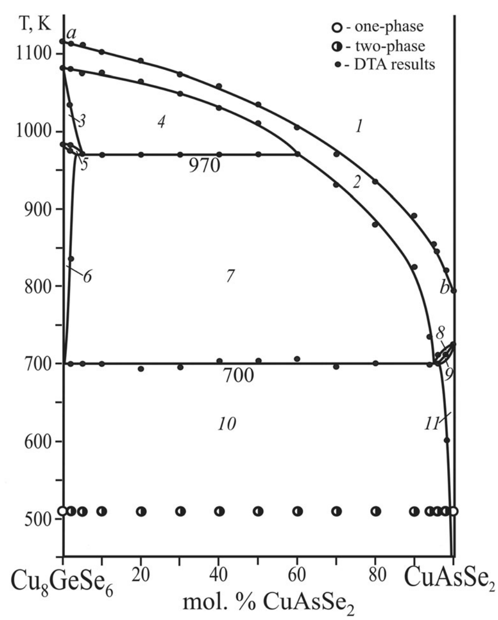

Fig. 4 The vertical section Cu_8GeSe_6-$CuAsSe_2$: 1-L, 2-L + γ, 3-γ + HTM-Cu_8GeSe_6, 4-L + γ + HTM-Cu_8GeSe_6, 5-HTM-Cu_8GeSe_6 + LTM-Cu_8GeSe_6 + γ, 6-LTM-Cu_8GeSe_6 + γ, 7-L + LTM-Cu_8GeSe_6 + γ, 8-L + γ + δ, 9-δ + γ, 10-LTM-Cu_8GeSe_6 + δ, 11-δ (where γ-solid solutions of Cu_2Se, δ-solid solutions of $CuAsSe_2$)

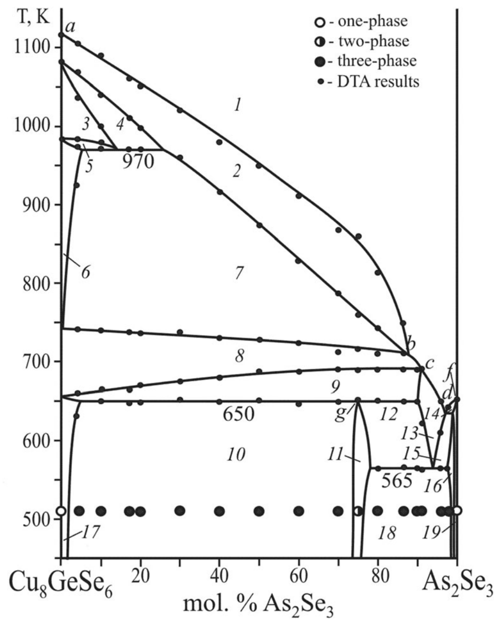

Fig. 5 The vertical section Cu_8GeSe_6-As_2Se_3: 1-L, 2-L + γ, 3-HTM-Cu_8GeSe_6 + γ, 4-L + γ + HTM-Cu_8GeSe_6, 5-HTM-Cu_8GeSe_6 + LTM-Cu_8GeSe_6 + γ, 6-γ + LTM-Cu_8GeSe_6, 7-L + γ + LTM-Cu_8GeSe_6, 8-L + LTM-Cu_8GeSe_6, 9-L + δ + LTM-Cu_8GeSe_6, 10-LTM-Cu_8GeSe_6 + η + δ, 11-η + δ, 12-L + η + δ, 13-L + δ, 14-L + β, 15-L + δ + β, 16-δ + β, 17-LTM-Cu_8GeSe_6 + δ, 18-δ + η + β, 19-β (where β-solid solutions of As_2Se_3, γ-solid solutions of Cu_2Se, δ-solid solutions of $CuAsSe_2$)

converges to this plane. The alloy 25 mol.% Cu_8GeSe_6-75 mol.% As_2Se_3 is two-phase according to XRD (Fig. 5) because the nonvariant process L_{U2} + LTM-Cu_8GeSe_6 ↔ η + δ at point *g* ends with the exhaustion of both liquid and the crystals of LTM-Cu_8GeSe_6, so the field 11 is two-phase. This field separates two three-phase regions of the co-existence of LTM-Cu_8GeSe_6, δ, η phases (field 10) and of the monovariant eutectic process L ↔ δ +η (field 12). The latter it ends at the plane of nonvariant eutectic process L_{E1}↔ δ + η + β at 565 K (292 °C). The field of another monovariant eutectic process L ↔ δ + β (field 15) also converges to this plane. Below this plane the alloys are three-phase, δ + η + β (field 18).

3.6 The Vertical Section *A–B* (*A*: 85 mol.% $GeSe_2$-15 mol.% Cu_2Se; *B*: 85 mol.% As_2Se_3-15 mol.% Cu_2Se)

The section *A–B* was investigated by DTA and XRD methods (Fig. 6). The section liquidus consists of the curves *ab* of the primary crystallization of α-solid solutions of $GeSe_2$, *bc* (η-solid solutions of Cu_2GeSe_3), *cd* (δ-solid solutions of $CuAsSe_2$). The vertical section crosses two subsystems of the quasi-ternary system Cu_2Se-$GeSe_2$-As_2Se_3. In the $GeSe_2$-Cu_2GeSe_3-As_2Se_3 subsystem, the section

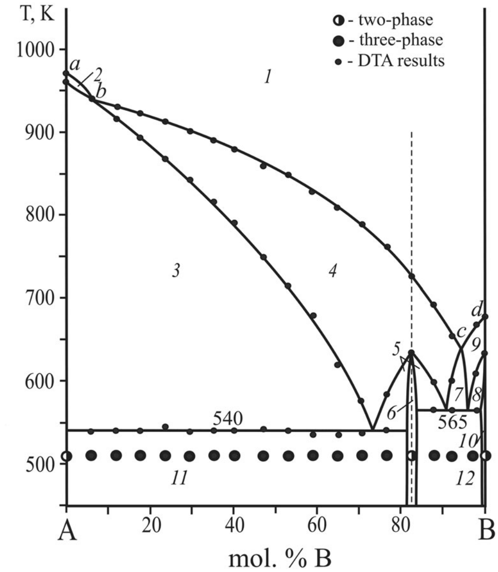

Fig. 6 The vertical section *A–B* (*A*: 85 mol.% $GeSe_2$-15 mol.% Cu_2Se; *B*: 85 mol.% $GeSe_2$-15 mol.% Cu_2Se): 1-L, 2-L + α, 3-L + α + η, 4-L + η, 5-L + η + β, 6-η + β, 7-L + η + δ, 8-L + β + δ, 9-L + δ, 10-δ + β, 11-η + α + β, 12-η + δ + β (where α-solid solutions of $GeSe_2$, β-solid solutions of As_2Se_3, γ-solid solutions of Cu_2Se, δ-solid solutions of $CuAsSe_2$)

crosses the plane of nonvariant eutectic process L_{E2}↔ α + η + β at 540 K (267 °C). The nonvariant eutectic process L_{E1}↔ η + δ + β takes place in the Cu_2GeSe_3-As_2Se_3-Cu_2Se subsystem at 565 K (292 °C). The samples below the planes of these processes are three-phase (fields 11, 12). These three-phase regions are separated by two-phase field 6, the existence of which is caused by the intersection with the quasi-binary system Cu_2GeSe_3-As_2Se_3. Monovariant eutectic processes L ↔ α + η and L ↔ η + β converges onto the plane of the nonvariant process at 540 K (267 °C). Monovariant eutectic processes L ↔ η + β (field 5), L ↔ η + δ (field 7), L ↔ β + δ (field 8) converges to the plane of the nonvariant eutectic process at 565 K (292 °C). The phase composition at the annealing temperature of 513 K (240) was determined by x-ray phase analysis (Fig. 6).

3.7 Isothermal Section of the Quasi-Ternary System Cu_2Se-$GeSe_2$-As_2Se_3 at 513 K (240 °C)

Based on the results of x-ray diffraction and MSA of the 137 samples (Fig. 7) the isothermal section of the system at 513 K (240 °C) was plotted (Fig. 8). It was investigated, that binary compounds crystallizes: Cu_2Se in space group *C*2/*c*, *a* = 0.7135(2) nm, *b* = 1.2383(1) nm, *c* = 2.7387(4) nm, *β* = 94.307(2); $GeSe_2$ in space group $P2_1/c$, *a* = 0.7007(2) nm, *b* = 1.6819(5) nm, *c* = 1.1806(3) nm, *β* = 90.74(2); As_2Se_3 in space group $P2_1/c$, *a* = 0.4267(2) nm, *b* = 0.9874(5) nm, *c* = 1.2794(7) nm,

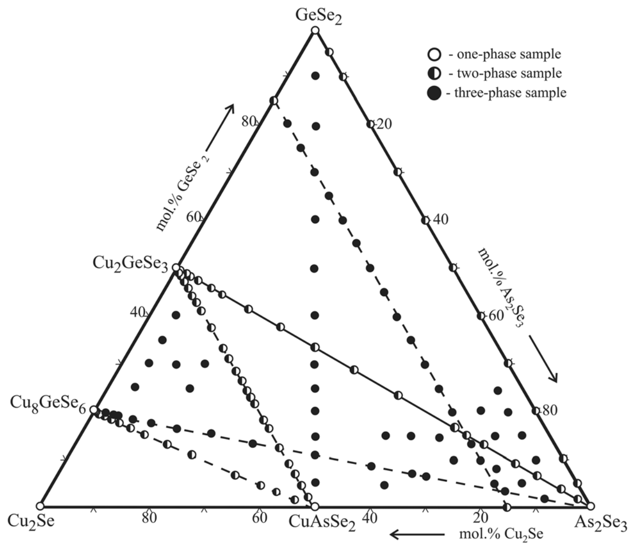

Fig. 7 Chemical and phase compositions of the Cu_2Se-$GeSe_2$-As_2Se_3 system samples at 513 K

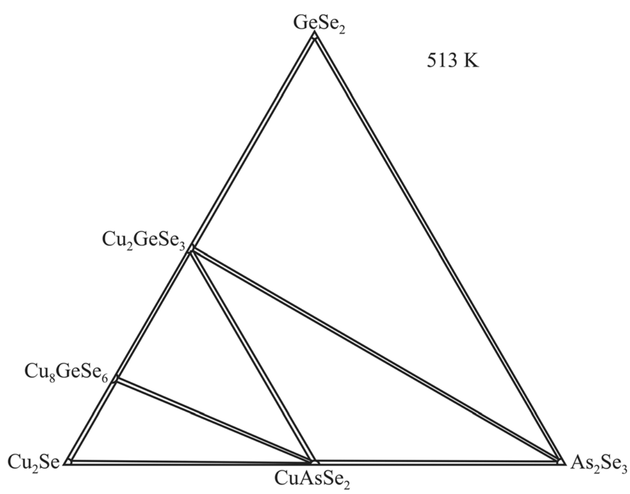

Fig. 8 The isothermal section of the quasi-ternary system Cu_2Se-$GeSe_2$-As_2Se_3 at 513 K

α = 109.96(4), what is in good agreement with literature data [19] for Cu_2Se, [20] for $GeSe_2$ and [21] for As_2Se_3. The existence of the three ternary compounds Cu_8GeSe_6, Cu_2GeSe_3 and $CuAsSe_2$ was confirmed. Diffractograms of the ternary compounds were indexed: Cu_2GeSe_3 in space group *Imm2*, *a* = 1.1859(1) nm, *b* = 0.3951(4) nm, *c* = 0.54879(2) nm; Cu_8GeSe_6 in space group $P6_3cm$, *a* = 1.26421(2) nm, *c* = 1.17567(3) nm; $CuAsSe_2$ in space group *R3* ($Cu_7As_6Se_{13}$ structure type) with the cell parameters *a* = 1.4014(2) nm, *c* = 0.9583(3) nm, what is in good agreement with literature data.[8,9,14]

The quasi-ternary system is divided into 4 subsystems: Cu_2Se-Cu_8GeSe_6-$CuAsSe_2$; Cu_8GeSe_6-$CuAsSe_2$-Cu_2GeSe_3; $CuAsSe_2$-Cu_2GeSe_3-As_2Se_3, and Cu_2GeSe_3-$GeSe_2$-As_2Se_3. No extensive solid solutions were found, and the solid solubility based on binary and ternary compounds is less than 2 mol.%.

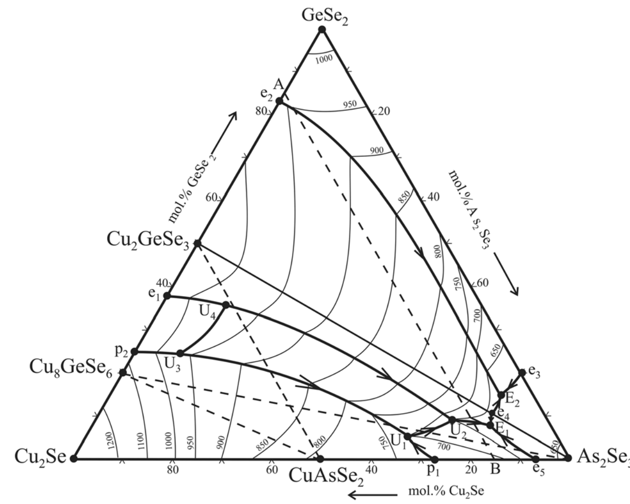

Fig. 9 Liquidus surface projection of the quasi-ternary system Cu_2Se-$GeSe_2$-As_2Se_3

3.8 Liquidus Surface Projection of the Quasi-Ternary System Cu_2Se-$GeSe_2$-As_2Se_3

Liquidus surface projection of the Cu_2Se-$GeSe_2$-As_2Se_3 system (Fig. 9 and Table 1) was plotted using the literature data,[7,10] the experimental results of the study of four vertical sections, two phase diagrams and additional samples to find out the nonvariant points (Fig. 9). The liquidus surface consists of the fields of the primary crystallization of γ-solid solutions of Cu_2Se, δ-solid solutions of $CuAsSe_2$, HTM-Cu_8GeSe_6, LTM-Cu_8GeSe_6, η-solid solutions of Cu_2GeSe_3 (the largest field), α-solid solutions of $GeSe_2$, and β-solid solutions of As_2Se_3. The fields are separated by 11 monovariant curves and 13 nonvariant points. The Cu_2GeSe_3-As_2Se_3 section is quasi-binary and divides the studied system into two subsystems, Cu_2Se-Cu_2GeSe_3-As_2Se_3 and As_2Se_3-Cu_2GeSe_3-$GeSe_2$. Point U_1 lies on the plane of the nonvariant peritectic process $L_{U1} + \gamma \leftrightarrow \delta +$ LTM-Cu_8GeSe_6 that takes place at 700 K (427 °C). Point U_2 belongs to the plane of the nonvariant peritectic process $L_{U2} +$ LTM-$Cu_8GeSe_6 \leftrightarrow \eta + \delta$ at 650 K (377 °C). The lines of monovariant eutectic equilibria $L_{U2\text{-}E1} \leftrightarrow \eta + \delta$, $L_{e5\text{-}E1} \leftrightarrow \delta + \beta$, $L_{e4\text{-}E1} \leftrightarrow \eta + \beta$ converge to the point E_1 of the nonvariant eutectic process $L_{E1} \leftrightarrow \eta + \delta + \beta$ at 565 K (292 °C). The points U_3 and U_4 lie on the planes of the isothermal processes HTM-$Cu_8GeSe_6 \leftrightarrow$ LTM-$Cu_8GeSe_6 + \gamma + L_{U3}$ and HTM-$Cu_8GeSe_6 \leftrightarrow$ LTM-$Cu_8GeSe_6 + \eta + L_{U4}$ at 970 K which exist due to polymorphic transformation of HTM-Cu_8GeSe_6 into LTM-Cu_8GeSe_6 in the Cu_2Se-$GeSe_2$ quasi-binary system. In the As_2Se_3-Cu_2GeSe_3-$GeSe_2$ subsystem

Table 1 Character, temperatures of nonvariant processes and coordinates of nonvariant points of the quasi-ternary system Cu_2Se-$GeSe_2$-As_2Se_3

Nonvariant point	Process	T, K (T, °C)	Composition, mol.%		
			Cu_2Se	$GeSe_2$	As_2Se_3
e_1	$L \leftrightarrow$ HTM-$Cu_8GeSe_6 + \eta$	1033 (760)	62	38	…
e_2	$L \leftrightarrow \eta + \alpha$	960 (687)	17	83	…
e_3	$L \leftrightarrow \alpha + \beta$	618 (345)	…	20	80
e_4	$L \leftrightarrow \eta + \beta$	633 (360)	10.5	10.5	79
e_5	$L \leftrightarrow \delta + \beta$	633 (360)	7	…	93
p_1	$L + \gamma \leftrightarrow \delta$	725 (452)	27	…	73
p_2	$L + \gamma \leftrightarrow$ HTM-Cu_8GeSe_6	1083 (810)	75	25	…
U_1	$L_{U1} + \gamma \leftrightarrow \delta +$ LTM-Cu_8GeSe_6	700 (427)	30	5	65
U_2	L_{U2} + LTM-$Cu_8GeSe_6 \leftrightarrow \delta + \eta$	650 (377)	19	9	72
U_3	HTM-$Cu_8GeSe_6 \leftrightarrow$ LTM-$Cu_8GeSe_6 + \gamma + L_{U3}$	970 (697)	66	24.5	9.5
U_4	HTM-$Cu_8GeSe_6 \leftrightarrow$ LTM-$Cu_8GeSe_6 + \eta + L_{U4}$	970 (697)	51	36	13
E_1	$L_{E1} \leftrightarrow \beta + \delta + \eta$	565 (292)	12	8	80
E_2	$L_{E2} \leftrightarrow \beta + \eta + \alpha$	540 (267)	7	15	78

one nonvariant eutectic process $L_{E2} \leftrightarrow \alpha + \eta + \beta$ takes place at 540 K (267 °C). The curves of monovariant eutectic processes $L_{e2-E2} \leftrightarrow \eta + \alpha$, $L_{e3-E2} \leftrightarrow \alpha + \beta$, $L_{e4-E2} \leftrightarrow \eta + \beta$ converge to the point E_2.

4 Conclusions and Future Work

The component interaction in the Cu_2Se-$GeSe_2$-As_2Se_3 system has been investigated by direct synthesis, x-ray phase and differential thermal analysis methods. For the first time phase equilibria in the quasi-ternary system have been investigated, and the triangulation of the system has been performed at 513 K (240 °C). At this temperature the existence of six single-phase fields has been identified based on the components $GeSe_2$, As_2Se_3, Cu_2Se of the system and the ternary compounds Cu_2GeSe_3, Cu_8GeSe_6, $CuAsSe_2$. The liquidus surface projection of the Cu_2Se-$GeSe_2$-As_2Se_3 quasi-ternary system has been built based on the literary and obtained results of the investigations of the vertical sections Cu_2GeSe_3-$CuAsSe_2$, Cu_8GeSe_6-$CuAsSe_2$, Cu_8GeSe_6-As_2Se_3, *A*–*B* (*A* = 85 mol.% $GeSe_2$-15 mol.% Cu_2Se; *B* = 85 mol.% As_2Se_3-15 mol.% Cu_2Se) and two phase diagrams $GeSe_2$-As_2Se_3 and Cu_2GeSe_3-As_2Se_3. The liquidus surface projection consists of fields of primary crystallization of γ-solid solutions of Cu_2Se, δ-solid solutions of $CuAsSe_2$, η-solid solutions of Cu_2GeSe_3, α-solid solutions of $GeSe_2$ and β-solid solutions of As_2Se_3, and HTM-Cu_8GeSe_6, LTM-Cu_8GeSe_6. They are separated by 11 monovariant curves and 12 nonvariant points. Six nonvariant processes take place in the Cu_2Se-$GeSe_2$-As_2Se_3 system: $L_{U1} + \gamma \leftrightarrow \delta +$ LTM-Cu_8GeSe_6 at 700 K (427 °C), L_{U2} + LTM-$Cu_8GeSe_6 \leftrightarrow \eta + \delta$ at 650 K (377 °C), $L_{E1} \leftrightarrow \eta + \delta + \beta$ at 565 K (292 °C), $L_{E2} \leftrightarrow \alpha + \eta + \beta$ at 540 K (267 °C), the points U_3 and U_4 lie on the planes of the isothermal processes HTM-$Cu_8GeSe_6 \leftrightarrow$ LTM-$Cu_8GeSe_6 + \gamma + L_{U3}$ and HTM-$Cu_8GeSe_6 \leftrightarrow$ LTM-$Cu_8GeSe_6 + \eta + L_{U4}$ at 970 K which exist due to polymorphic transformation of HTM-Cu_8GeSe_6 into LTM-Cu_8GeSe_6 in the Cu_2Se-$GeSe_2$ quasi-binary system.

This work was performed in order to gather more data for a thermodynamic assessment of the Cu_2Se-$B^{IV}Se_2$-As_2Se_3 systems, where B^{IV}-Si, Ge, Sn, which is currently in progress.

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