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Quasi-Ternary System Cu_2S-HgS-SnS_2

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Abstract Phase equilibria in the quasi-ternary system Cu_2S-HgS-SnS_2 were studied by physico-chemical analysis methods on 152 alloys that were synthesized by direct single-temperature method. Phase diagrams of the quasi-binary system Cu_2S-HgS, six vertical sections (Cu_2S-Cu_2HgSnS_4, Cu_2SnS_3-HgS, Cu_2HgSnS_4-SnS_2, $Cu_2Sn_4S_9$-Cu_2HgSnS_4, Cu_4SnS_4-Cu_2HgSnS_4, A–B (A—40 mol.% HgS, 60 mol.% Cu_2S; B—40 mol.% HgS, 60 mol.% SnS_2), liquidus surface projection, and isothermal section at 670 K were investigated. The coordinates of eutectic points were determined: 59 mol.% HgS, 983 K (in the Cu_2S-HgS system); 73 mol.% Cu_2S, 1060 K (at the Cu_2S-Cu_2HgSnS_4 section); 18 mol.% HgS, 1113 K and 88 mol.% HgS, 1035 K (at the Cu_2SnS_3-HgS section); 83 mol.% SnS_2, 1021 K (at the Cu_2HgSnS_4-SnS_2 section).

Keywords isothermal section · liquidus surface projection · phase diagram · quasi-ternary system · quasi-binary section · vertical section

1 Introduction

Investigation of phase equilibria in the Cu_2S-HgS-SnS_2 system is part of the systematic study of quasi-ternary systems Cu_2X-$B^{II}X$-$D^{IV}X_2$ (B^{II}-Zn, Cd, Hg; D^{IV}-Si, Ge, Sn; X-S, Se) and the crystal structure of compounds which formed in the systems. Binary system components Cu_2S, HgS and SnS_2 melt congruently at 1401 K,[1] 1098 K,[2] and 1143 K,[3] respectively, and have narrow homogeneity regions near the stoichiometric composition.

The Cu_2S-HgS-SnS_2 system features the Cu_2HgSnS_4 compound which is a direct-band semiconductor. Cu_2HgSnS_4 has properties suitable for optoelectronic devices and absorbing layer of thin-film solar cells[4] but any possible use would be severely limited due to the toxicity of mercury.

2 Quasi-binary Systems

2.1 Cu_2S-SnS_2 Systems

The results of the studies of the Cu_2S-SnS_2 system were published in Ref 5–10. According to Ref 10, three ternary compounds form in the system, Cu_4SnS_4, Cu_2SnS_3 and $Cu_2Sn_4S_9$. The Cu_2SnS_3 compound has a natural analog, the mochite mineral[9].

According to Ref 6, in addition to the above compounds, the ternary phase $Cu_4Sn_3S_8$ was found in the Cu_2S-SnS_2 system. Cu_2SnS_3 melts congruently at 1123 K. Compounds Cu_4SnS_4 and $Cu_2Sn_4S_9$ formed in solid-state reactions $Cu_2SnS_3 + Cu_2S \Leftrightarrow Cu_4SnS_4$ and $Cu_4Sn_3S_8 + 5SnS_2$ - $2Cu_2Sn_4S_9$ at 1083 and 938 K, respectively. $Cu_4Sn_3S_8$ is formed by the peritectic reaction L + $Cu_2SnS_3 \Leftrightarrow Cu_4Sn_3S_8$ and exists in the temperature range 658–1063 K. There are three invariant points in the system, two eutectics and one peritectic, with the coordinates 31 mol.% SnS_2 and 1093 K, 77 mol.% SnS_2 and 1043 K, 70 mol.% SnS_2 and 1063 K, respectively.

According to Ref 5, three phases were found in the Cu_2S-SnS_2 system, Cu_2SnS_3, $Cu_2Sn_4S_9$ and Cu_8SnS_6. The

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formation of the first two compounds occurs as described in Ref 6. The difference is in the value of the melting point of Cu_2SnS_3 which according to Ref 5 is 1173 K. Cu_8SnS_6 is formed by the solid-state reaction $3Cu_2S + Cu_2SnS_3$ - Cu_8SnS_6 at 1083 K. The solid solutions range of Cu_2S, SnS_2 and ternary compounds are 2 mol.% or less.

Given existing contradictions in the literature, the authors of Ref 11 re-investigated the Cu_2S-SnS_2 system in detail. The authors report the existence of three compounds, Cu_2SnS_3 which melts congruently at 1133 K, Cu_4SnS_4, formed by the solid-state reaction of $Cu_2SnS_3 + Cu_2S \Leftrightarrow Cu_4SnS_4$ at 1083 K, and $Cu_2Sn_4S_9$ formed by the reaction $Cu_2SnS_3 + 3SnS_2 \Leftrightarrow Cu_2Sn_4S_9$ at 943 K (closely agreeing in this regard to Ref 6). The existence of $Cu_4Sn_3S_8$ and $CuSn_{3.75}S_8$ compounds was not confirmed. The solid solubility based on the starting components does not exceed 2 mol.%. Polymorphous transformations of Cu_2S result in solid-state processes at 656 and 381 K.

2.2 HgS-SnS$_2$ System

The Hg_S-SnS_2 system is a quasi-binary section of the ternary system Hg-Sn-S[12] and belongs to the eutectic type. The eutectic coordinates are 920 K and 48 mol.% HgS. The solid solution ranges of the binary compounds at 700 K are 0–2 and 99–100 mol.% SnS_2.

2.3 Cu$_2$S-HgS Systems

The Cu_2S-HgS system was studied in Ref 13, 14. According to Ref 13, the Cu_2S-HgS system is a quasi-binary section of the ternary system Cu-Hg-S and exhibits eutectic type of interaction. The eutectic coordinates are 963 K and 58 mol.% HgS[13] or 976 K and 74 mol.% HgS.[14]

Crystallographic characteristics of binary, ternary and quaternary chalcogenides of the quasi-ternary system Cu_2S-HgS-SnS_2 are gathered in Table 1.

3 Experimental

The compounds and alloys of the studied system were synthesized from semiconductor-purity elements (Cu, Ge and S) and pre-synthesized HgS. Sulfur and mercury were further purified by vacuum distillation before use. Due to the high vapor pressure of the components, the synthesis of HgS was performed in an evacuated quartz container with thickened walls. Stoichiometric amounts of starting elements were used for the synthesis. At the first stage the ampoule was heated to 473 K at the rate of 30–40 K/h. The heating to the maximum temperature of 873 K was held at the rate of 5–10 K/h. After annealing for 48 hours, the container with synthesized HgS was cooled to room temperature at the rate of 10–15 K/h.

The calculated amounts of starting components were loaded into quartz ampoules that were evacuated to residual pressure of 10^{-2} Pa and soldered.

Based on the p-T diagrams of the starting materials, single-temperature method was selected for the synthesis of alloys. The synthesis was performed in commercial programmable furnaces. The temperature was raised at the rate of 20–30 K/h to the maximum of 1400 K, with 4 h stays at the melting points of the batch components. The alloys were then cooled at the rate of 10–20 K/h to 670 K where homogenizing annealing at was held for 500 h. Annealed alloys were quenched into 25% aqueous NaCl solution.

Differential thermal analysis utilized a Paulik–Paulik–Erdei derivatograph, with Pt/Pt-Rh thermocouple and Al_2O_3 as a standard. All static parameters were stable during the experiment. X-ray phase analysis using WinCSD software package[24] was performed on diffraction patterns recorded at a DRON 4-13 diffractometer (CuKα-radiation). Microstructural analysis was performed using an MMU-3 metal microscope.

3.1 Quasi-ternary System Cu$_2$S-HgS-SnS$_2$

Phase equilibria in the quasi-ternary system Cu_2S-HgS-SnS_2 were studied on 152 alloys the chemical and phase composition of which is shown in Fig. 1.

3.2 Characteristics of Quasi-binary Boundary Systems of the Quasi-ternary System

Ambiguous data regarding the melting point and coordinates of the eutectic point led to reinvestigation of the phase equilibria in the Cu_2S-HgS system.

The phase diagram of this system in the entire concentration range is shown in Fig. 2. The Cu_2S-HgS system is a quasi-binary section of the ternary system Cu-Hg-S. The eutectic of the section components has the coordinates of 59 mol.% HgS (δ') and 983 K. The solid solution range of HT-modification of Cu_2S (γ'') extends to 52 mol.% HgS at the eutectic temperature and decreases with decreasing temperature.

The presence of three polymorphous modifications of Cu_2S and one polymorphous transition of HgS determines the complex nature of phase formation in the sub-solidus part of the diagram where there are two eutectoid ($\delta' \Leftrightarrow \gamma'' + \delta$ at 587 K and $\gamma'' \Leftrightarrow \gamma' + \delta$ at 524 K) and one peritectoid ($\gamma' + \delta \Leftrightarrow \gamma$ at 386 K) processes. Literature data on the investigation of the Cu_2S-SnS_2 and HgS-SnS_2 systems were used in the construction of the liquidus

Table 1. Crystallographic parameters of the compounds

Compound	SG	Lattice parameters, nm	References
γ-Cu_2S	$P2_1/c$	$a = 1.5246$, $b = 1.1884$, $c = 1.3494$, $\beta = 116.35°$	15
γ′-Cu_2S*	$P6_3/mmc$	$a = 0.395$, $c = 0.675$	15
γ″-Cu_2S	$Fm\bar{3}m$	$a = 0.545$	16
δ-HgS	P3221	$a = 0.4074$, $c = 0.9395$	17
δ′-HgS*	$F\bar{4}3m$	$a = 0.58514$	18
SnS_2	$P\bar{3}ml$	$a = 0.3646$, $c = 0.5869$	19
Cu_4SnS_4	$Pnma$	$a = 1.3558$, $b = 0.7681$, $c = 0.6412$	20
Cu_2SnS_3	$I\bar{4}2m$	$a = 0.5413$, $c = 1.0824$	21
Cu_2SnS_3	Cc	$a = 0.6653$, $b = 1.1537$, $c = 0.6665$, $\beta = 109.39°$	22
$Cu_2Sn_4S_9$	$F4_132$	$a = 0.1040$	6
Cu_2HgSnS_4	$I\bar{4}2m$	$a = 0.5555$, $c = 1.0911$	23

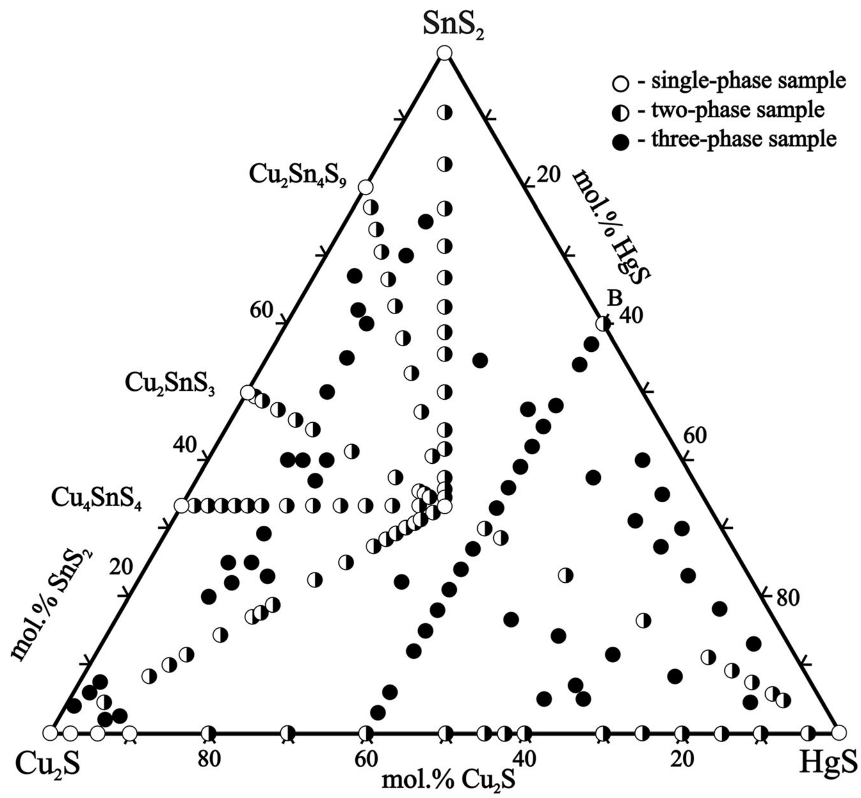

Fig. 1. Chemical and phase compositions of the Cu_2S-HgS-SnS_2 system alloys at 670 K

surface projection and isothermal section of the quasi-ternary system Cu_2S-HgS-SnS_2 at 670 K.

3.3 Quasi-binary System Cu_2S-Cu_2HgSnS_4

The Cu_2S-Cu_2HgSnS_4 section shown in Fig. 3 is a quasi-binary section of the quasi-ternary subsystem Cu_2SnS_3-HgS-Cu_2S and belongs to the eutectic type. The eutectic process L ⇔ Cu_2HgSnS_4 + γ″ takes place at 1060 K, and the eutectic point has composition of 73 mol.% Cu_2S.

The solid solubility in HT-Cu_2S modification (γ″-solid solutions) at 1060 K does not exceed 18 mol.% Cu_2HgSnS_4 and decreases with decreasing temperature. At the annealing temperature, the solid solubility of Cu_2HgSnS_4 in γ″ does not exceed 3 mol.% Cu_2HgSnS_4. The solid solubility based on Cu_2HgSnS_4 is less than 2 mol.% Cu_2S.

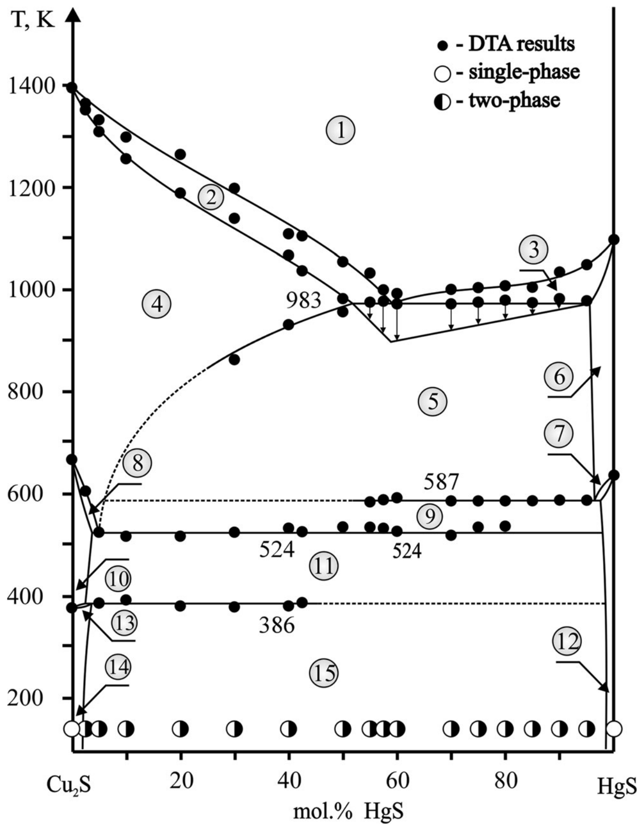

Fig. 2. Phase diagram of the Cu_2S-HgS system: 1 – L, 2 – L + γ'', 3 – L + δ', 4 – γ'', 5 – γ'' + δ', 6 – δ', 7 – δ + δ', 8 – γ'' + γ', 9 – γ'' + δ, 10 – γ', 11 – γ' + δ, 12 – δ, 13 – γ' + γ, 14 – γ, 15 – γ + δ

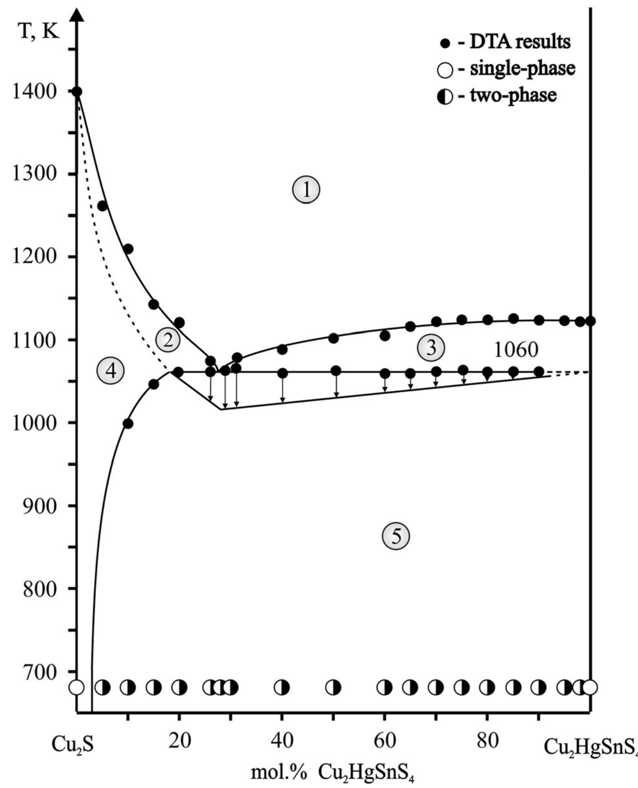

Fig. 3. Phase diagram of the Cu_2S-Cu_2HgSnS_4 system: 1 – L, 2 – L + γ'', 3 – L + Cu_2HgSnS_4, 4 – γ'', 5 – γ'' + Cu_2HgSnS_4

3.4 Quasi-binary System Cu_2SnS_3-HgS

Phase diagram of the Cu_2SnS_3-HgS section plotted from the results of physico-chemical analysis is shown in Fig. 4. The system is a quasi-binary section of the quasi-ternary system Cu_2S-HgS-SnS_2. The Cu_2HgSnS_4 (ε) compound which melts congruently at 1122 K is formed in the system at the 1:1 ratio of the section components. The maximum melting point of the quaternary compound is shifted towards the ternary phase Cu_2SnS_3 (χ).

The diffraction pattern of Cu_2HgSnS_4 was indexed well in the tetragonal symmetry (stannite structural type, SG $I\bar{4}2m$) with unit cell parameters $a = 0.5580(2)$ nm: $c = 1.0895(3)$ nm. The ternary compound Cu_2SnS_3 crystallizes in the sphalerite structure (SG, $a = 0.54276(2)$ nm).

The interaction of Cu_2HgSnS_4 with the section components is eutectic. The eutectics melt at 1113 K and 1035 K and have the composition of 18 and 88 mol.% HgS, respectively. The solid solubility in the section components at the annealing temperature is less than 2 mol.%.

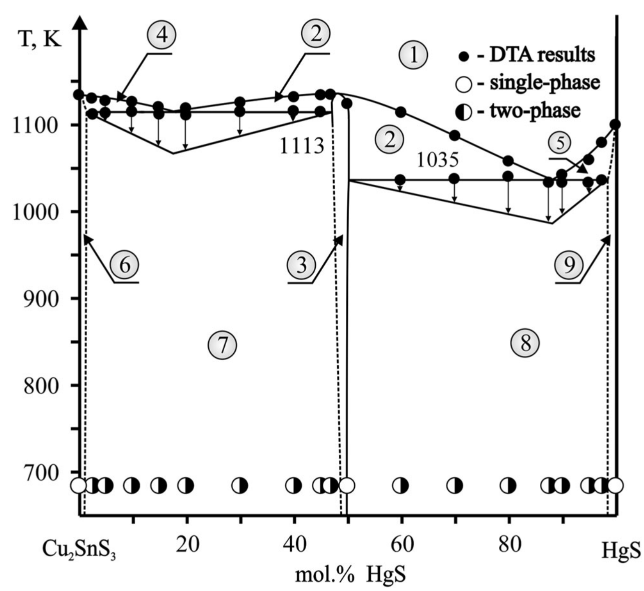

Fig. 4. Phase diagram of the Cu_2SnS_3-HgS system: 1 – L, 2 – L + ε, 3 – ε, 4 – L + χ, 5 – L + δ', 6 – χ, 7 – χ + ε, 8 – ε + δ', 9 – δ'

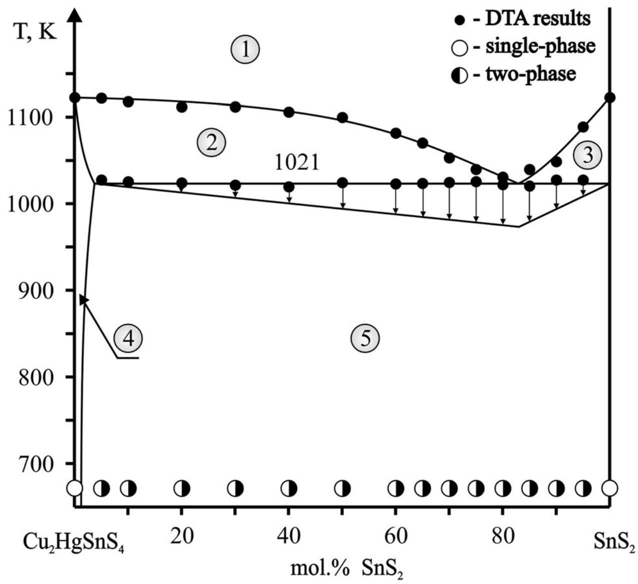

Fig. 5. Phase diagram of the Cu_2HgSnS_4-SnS_2 system: 1 – L 2 – L + ε, 3 – L + SnS_2, 4 – ε, 5 – ε + SnS_2

3.5 Quasi-binary System Cu_2HgSnS_4-SnS_2

Phase diagram of the Cu_2HgSnS_4-SnS_2 section based on the results of DTA, XRD and microstructure analysis is shown in Fig. 5. The section is quasi-binary, with the eutectic nature of interaction. The eutectic reaction L ⇔ ε + SnS_2 takes place at 1021 K, the composition of the eutectic point is 83 mol.% SnS_2. The solid solubility based on the section components is negligible.

3.6 Vertical Section $Cu_2Sn_4S_9$-Cu_2HgSnS_4

The section liquidus consists of two curves of the primary crystallization of the ternary Cu_2SnS_3 and quaternary Cu_2HgSnS_4 compounds (Fig. 6). The secondary crystallization is represented by the binary eutectics Cu_2SnS_3 + SnS_2 (field 4) and Cu_2HgSnS_4 + Cu_2SnS_3 (field 5).

The horizontal line at 1015 K corresponds to the ternary invariant eutectic process L ⇔ SnS_2 + Cu_2SnS_3 + ε which has at this section an excess of SnS_2 and Cu_2SnS_3. The solid-state process SnS_2 + Cu_2SnS_3 ⇔ $Cu_2Sn_4S_9$ at 933 K results in all alloys of the section becoming two-phase at the annealing temperature 670 K except end components of the section $Cu_2Sn_4S_9$ and Cu_2HgSnS_4.

3.7 Vertical Section Cu_4SnS_4-Cu_2HgSnS_4

The liquidus of the Cu_4SnS_4-Cu_2HgSnS_4 section consists of two lines of the primary crystallization of the ternary Cu_2SnS_3 and quaternary Cu_2HgSnS_4 phases (Fig. 7). The horizontal line at 1083 K corresponds to the four-phase peritectic process L + Cu_2SnS_3 + γ'' ⇔ Cu_4SnS_4.

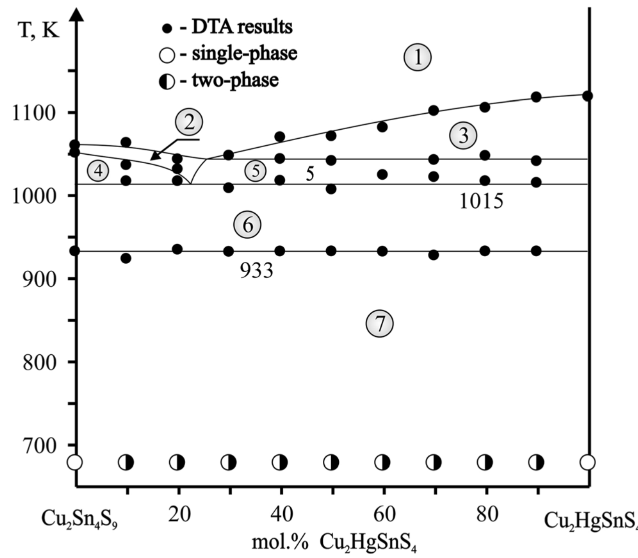

Fig. 6. Vertical section $Cu_2Sn_4S_9$-Cu_2HgSnS_4: 1 – L, 2 – L + Cu_2SnS_3, 3 – L + Cu_2HgSnS_4, 4 – L + SnS_2 + Cu_2SnS_3, 5 – L + Cu_2HgSnS_4 + SnS_2, 6 – Cu_2SnS_3 + SnS_2 + Cu_2HgSnS_4, 7 – $Cu_2Sn_4S_9$ + Cu_2HgSnS_4

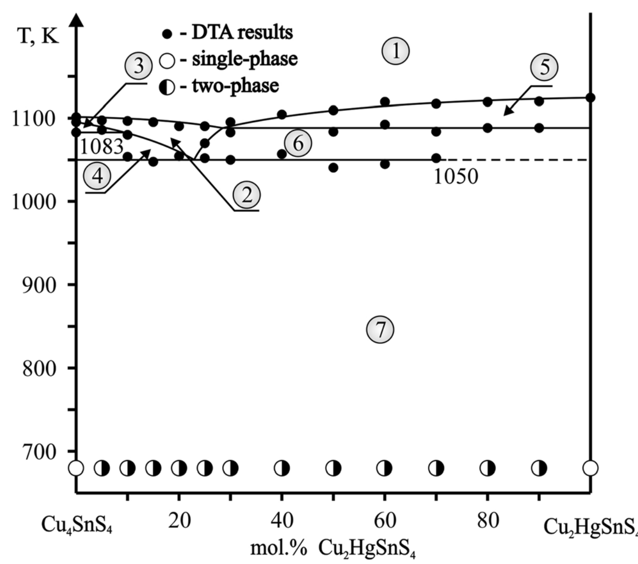

Fig. 7. Vertical section Cu_4SnS_4-Cu_2HgSnS_4: 1 – L, 2 – L + Cu_2SnS_3, 3 – L + γ'' + Cu_2SnS_3, 4 – L + Cu_4SnS_4 + α, 5 – L + ε, 6 – ε + α, 7 – Cu_4SnS_4 + ε

3.8 Vertical Section A–B (A—60 mol.% Cu_2S; 40 mol.% HgS; B—60 mol.% SnS_2; 40 mol.% HgS)

The A–B section (Fig. 8) crosses two subsystems, Cu_2S-HgS-Cu_2HgSnS_4 and HgS-SnS_2-Cu_2HgSnS_4. The section liquidus consists of three lines of the primary

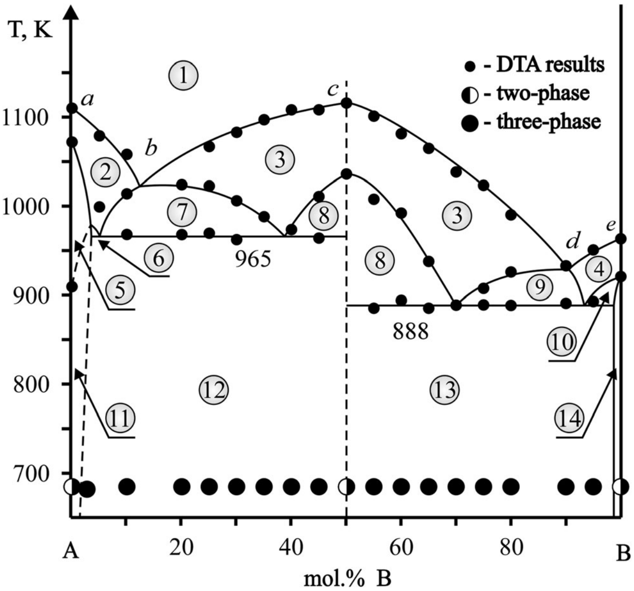

Fig. 8. Vertical section A–B: (A—60 mol.% Cu_2S; 40 mol.% HgS; B—60 mol.% SnS_2; 40 mol.% HgS): 1 – L, 2 – L + γ'', 3 – L + Cu_2HgSnS_4, 4 – L + SnS_2, 5 – γ'', 6 – L + γ'' + δ', 7 – L + γ'' + Cu_2HgSnS_4, 8 – L + Cu_2HgSnS_4 + δ', 9 – L + SnS_2 + Cu_2HgSnS_4, 10 – L + SnS_2 + δ', 11 – γ'' + δ', 12 – γ'' + Cu_2HgSnS_4 + δ', 13 – Cu_2HgSnS_4 + SnS_2 + δ', 14 – SnS_2

crystallization of γ''-solid solution range of HT-Cu_2S modification (part a–b), Cu_2HgSnS_4 (part b–d), and SnS_2 (part d–e).

The section solidus is formed by the boundary compositions of γ''- and δ'-solid solutions above the temperature of invariant processes and by the horizontal lines at 965 K and 888 K which belong to the eutectic processes $L \Leftrightarrow Cu_2HgSnS_4 + \gamma'' + \delta'$ and $L \Leftrightarrow Cu_2HgSnS_4 + SnS_2 + \delta'$.

The space between the liquidus and solidus lines, along with the fields of the primary crystallization volumes, contains the fields of the secondary crystallization $L \Leftrightarrow \gamma'' + Cu_2HgSnS_4$, $L \Leftrightarrow Cu_2HgSnS_4 + SnS_2$, and $L \Leftrightarrow Cu_2HgSnS_4 + \delta'$. Of all investigated alloys, three alloys with the content of 0, 50 and 100 mol.% B are two-phase in the subsolidus region; the remaining alloys contain three phases.

3.9 Liquidus Surface Projection of the Quasi-ternary System Cu_2S-HgS-SnS_2

Liquidus surface projection of the Cu_2S-HgS-SnS_2 system on the concentration triangle was plotted from the results presented above (Fig. 9). The liquidus consists of six fields of the primary crystallization of Cu_2S (γ''-solid solutions), HgS (δ'-solid solutions), SnS_2, Cu_2SnS_3, Cu_4SnS_4, and Cu_2HgSnS_4. They are separated by fourteen monovariant lines and fourteen invariant points, of which eight correspond to binary and six to ternary invariant processes. The nature and temperature of invariant processes are gathered in Table 2.

The Cu_2S-HgS-SnS_2 system is divided by the quasi-binary sections Cu_2SnS_3-HgS, Cu_2HgSnS_4-Cu_2S and Cu_2HgSnS_4-SnS_2 into four subsystems. The sub-systems Cu_2S-HgS-Cu_2HgSnS_4, HgS-SnS_2-Cu_2HgSnS_4 and SnS_2-Cu_2SnS_3-Cu_2HgSnS_4 are of the eutectic type.

The crystallization of alloys in the Cu_2S-Cu_2HgSnS_4-Cu_2SnS_3 system is more complex, due to the solid-state process of the formation of the ternary compound Cu_4SnS_4 ($\gamma'' + Cu_2SnS_3 \Leftrightarrow Cu_4SnS_4$) in the boundary system Cu_2S-SnS_2 at 1083 K. This is higher than the temperature of the eutectic process in the Cu_2S-Cu_2HgSnS_4 system (1060 K). Therefore, the ternary compound Cu_4SnS_4 has its own field of the primary crystallization on the liquidus surface, caused by the peritectic process $L + Cu_2SnS_3 + \gamma'' \Leftrightarrow Cu_4SnS_4$ which takes place at 1083 K.

3.10 Isothermal Section of the Quasi-ternary System Cu_2S-HgS-SnS_2 at 670 K

Isothermal section of the quasi-ternary system Cu_2S-HgS-SnS_2 at 670 K was plotted based on obtained results (Fig. 10). The quasi-binary systems Cu_2SnS_3-HgS, Cu_2HgSnS_4-SnS_2, Cu_2S-Cu_2HgSnS_4, and the $Cu_2Sn_4S_9$-Cu_2HgSnS_4 and Cu_4SnS_4-Cu_2HgSnS_4 sections which are quasi-binary in the sub-solidus part, separate the quasi-ternary system Cu_2S-SnS_2-HgS at 670 K into six subsystems. The quaternary compound Cu_2HgSnS_4 at the annealing temperature is in equilibrium with the components of the quasi-ternary system Cu_2S, HgS and SnS_2, as well as the ternary phases Cu_4SnS_4 and Cu_2SnS_3. The γ''-solid solution range of HT-Cu_2S modification is stretched at 670 K along the Cu_2S-HgS side. The solid solubility in Cu_2HgSnS_4, Cu_4SnS_4, Cu_2SnS_3, $Cu_2Sn_4S_9$, SnS_2, and HgS is negligible and does not exceed 2-3 mol.% at 670 K. Solid-state processes involving the $Cu_2Sn_4S_9$ compound should be noted in the Cu_2SnS_3-Cu_2HgSnS_4-SnS_2 subsystem. All alloys of this subsystem complete their crystallization in the ternary eutectic process $L \Leftrightarrow SnS_2 + Cu_2SnS_3 + Cu_2HgSnS_4$ at 1015 K. The quasi-binary section Cu_2S-SnS_2 features at 933 K the peritectoid process of the formation of the ternary phase $Cu_2Sn_4S_9$ ($Cu_2SnS_3 + SnS_2 \Leftrightarrow Cu_2Sn_4S_9$) which is stable at 670 K. This process takes also place in all alloys of the Cu_2SnS_3-Cu_2HgSnS_4-SnS_2 subsystem. The process ends with an excess of the ternary compound Cu_2SnS_3 in

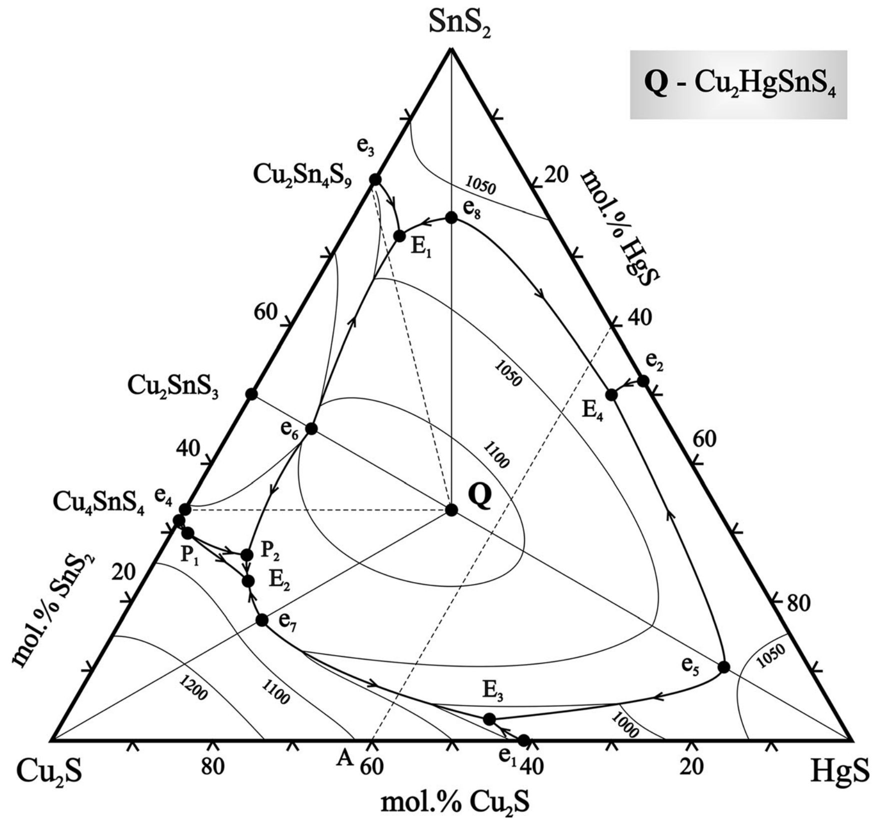

Fig. 9. Liquidus surface projection of the quasi-ternary system Cu_2S-HgS-SnS_2

Table 2. Character and temperature of invariant processes and coordinates of invariant points of the quasi-ternary system Cu_2S-HgS-SnS_2

Invariant point	Process	*T*, K	Composition, mol.%		
			Cu_2S	HgS	SnS_2
e_1	L ⇔ γ″ + δ′	983	41	59	…
e_2	L ⇔ SnS_2 + δ′	920	…	48	52
e_3	L ⇔ SnS_2 + Cu_2SnS_3	1061	19	…	81
e_4	L ⇔ γ″ + Cu_2SnS_3	1093	68	…	32
e_5	L ⇔ Cu_2HgSnS_4 + δ′	1035	11	78	11
e_6	L ⇔ Cu_2SnS_3 + Cu_2HgSnS_4	1113	45	10	45
e_7	L ⇔ Cu_2HgSnS_4 + γ″	1060	64	18	18
e_8	L ⇔ SnS_2 + Cu_2HgSnS_4	1021	13	13	74
E_1	L ⇔ Cu_2SnS_3 + SnS_2 + Cu_2HgSnS_4	1015	20	7	73
E_2	L ⇔ γ″ + Cu_2HgSnS_4 + Cu_4SnS_4	1045	64	13	23
E_3	L ⇔ γ″ + Cu_2HgSnS_4 + δ′	965	44	53	3
E_4	L ⇔ SnS_2 + Cu_2HgSnS_4 + δ′	888	5	45	50
P_1	L + Cu_2SnS_3 + γ″ ⇔ Cu_4SnS_4	1083	68	2	30
P_2	L + Cu_2SnS_3 ⇔ Cu_4SnS_4 + Cu_2HgSnS_4	1050	62	11	27

the Cu_2SnS_3-Cu_2HgSnS_4-$Cu_2Sn_4S_9$ part, with an excess of the binary compound SnS_2 in the $Cu_2Sn_4S_9$-Cu_2HgSnS_4-SnS_2 part, and only at the $Cu_2Sn_4S_9$-Cu_2HgSnS_4 section the process is completed stoichiometrically. The above solid-state processes lead to the emergence of the binary equilibrium Cu_2HgSnS_4-$Cu_2Sn_4S_9$ at the isothermal section.

4 Conclusions and Future Work

A total of 152 alloys were investigated by DTA, x-ray diffraction and MCA methods in the quasi-ternary system Cu_2S-HgS-SnS_2. Phase diagrams of the quasi-binary system Cu_2S-HgS, six vertical sections HgS-Cu_2SnS_3, Cu_2HgSnS_4-SnS_2, Cu_2S-Cu_2HgSnS_4, $Cu_2Sn_4S_9$-Cu_2HgSnS_4,

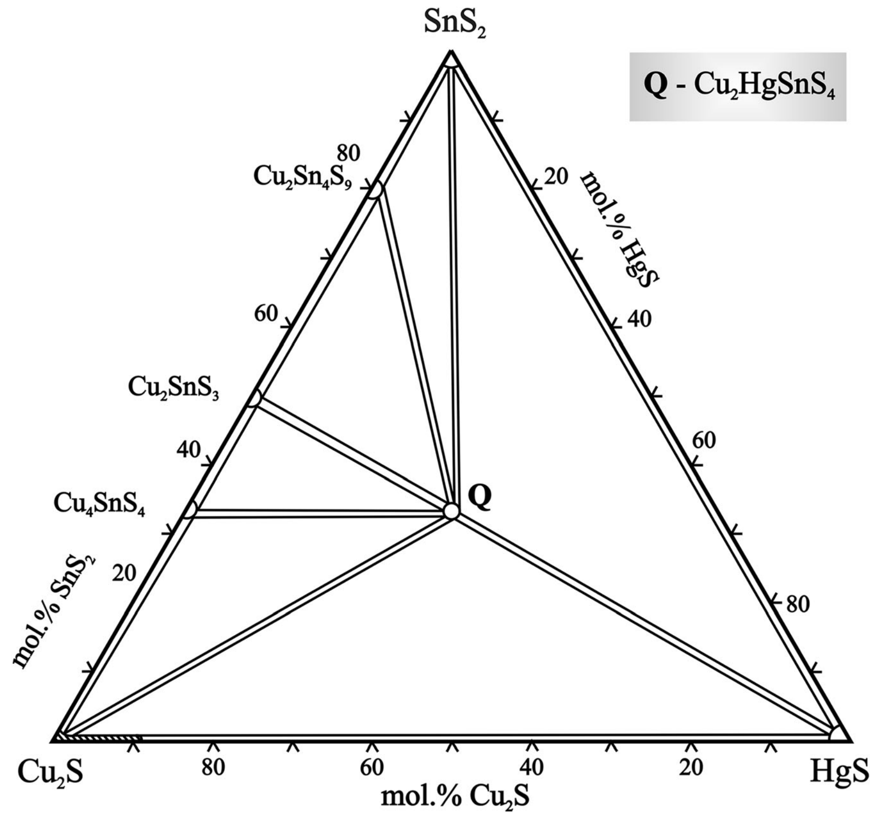

Fig. 10. Isothermal section of the quasi-ternary system Cu_2S-HgS-SnS_2 at 670 K

Cu_4SnS_4-Cu_2HgSnS_4, A–B (A—40 mol.% HgS, 60 mol.% Cu_2S; B—40 mol.% HgS, 60 mol.% SnS_2), liquidus surface projection onto the concentration triangle and isothermal section of the quasi-ternary system Cu_2S-HgS-SnS_2 at 670 K were investigated. The sections Cu_2HgSnS_4-SnS_2 and Cu_2S-Cu_2HgSnS_4 are quasi-binary systems of eutectic type with eutectic points coordinates 1021 K, 17 mol.% Cu_2HgSnS_4 and 1060 K, 27 mol.% Cu_2HgSnS_4, respectively. The existence of the quaternary compound Cu_2HgSnS_4 which melts congruently at 1122 K was found in the HgS-Cu_2SnS_3 system at the component ratio 1:1. The interaction of Cu_2HgSnS_4 with the section components is eutectic. The eutectics melt at 1113 K and 1035 K, eutectic points have composition of 18 and 88 mol.% HgS, respectively. The sections $Cu_2Sn_4S_9$-Cu_2HgSnS_4 and Cu_4SnS_4-Cu_2HgSnS_4 are quasi-binary only in the sub-solidus part due to the solid-state formation of ternary compounds. The Cu_2S-HgS-SnS_2 system is triangulated by quasi-binary sections into four subsystems. The coordinates of invariant points and positions of monovariant lines were established.

Presented results of the study of phase equilibria in the Cu_2S-HgS-SnS_2 system expand the database in the field of semiconductor materials science. Obtained results can be used to predict phase equilibria in analogous systems and in the development of technology for obtaining ternary and quaternary chalcogenides in the single-crystalline or polycrystalline state.

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