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PHASE EQUILIBRIA IN SYSTEMS $\text{Cu}_2\text{S} - \text{PbCuSbS}_3$ and $\text{CuSbS}_2 - \text{Pb}_5\text{Sb}_4\text{S}_{11}$ O.M.Aliyev, D.S.Ajdarova, T.F.Maksudova, V.M.Rahimova, T.A.Salimova
(Presented by Academician of ANAS A.M.Aliyev)

$\text{Cu}_2\text{S} - \text{PbCuSbS}_3$ and $\text{CuSbS}_2 - \text{Pb}_5\text{Sb}_4\text{S}_{11}$ systems were studied by physical and chemical analysis methods. It was determined that the section $\text{Cu}_2\text{S} - \text{PbCuSbS}_3$ is a quasibinary section of $\text{Cu}_2\text{S} - \text{PbS} - \text{Sb}_2\text{S}_3$ ternary system, and $\text{CuSbS}_2 - \text{Pb}_5\text{Sb}_4\text{S}_{11}$ is a non-quasibinary section. Phase equilibria in the $\text{Cu}_2\text{S} - \text{PbCuSbS}_3$ and $\text{CuSbS}_2 - \text{Pb}_5\text{Sb}_4\text{S}_{11}$ systems were investigated by physical-chemical analyses using DTA, X-ray phase, as well measurement of microhardness. T-x diagrams state have been plotted.

Keywords: eutectics, quasi-binary, solid solution

The objective of this research is the investigation of the character of chemical interaction in quasiternary system $\text{Cu}_2\text{S} - \text{PbS} - \text{Sb}_2\text{S}_3$ by the sections $\text{Cu}_2\text{S} - \text{PbCuSbS}_3$ and $\text{CuSbS}_2 - \text{Pb}_5\text{Sb}_4\text{S}_{11}$. The system $\text{CuSbS}_2 - \text{PbS}$ was studied earlier [1]. The system $\text{CuSbS}_2 - \text{PbS}$ is characterized by a complex chemical interaction. At 1:1 ratio of components quaternary sulfosalt is formed with PbCuSbS_3 which melt congruently at 1125K. PbCuSbS_3 forms eutectics with initial compounds. Coordinates of eutectic points: 20 mol% PbS and 675K, 70 mol% PbS and 950K. Solubility on the basis of ternary compound CuSbS_2 is found to be 6mol% based on lead sulphide. Homogeneity region was not practically observed. Quaternary sulfosalt PbCuSbS_3 is a phase of variable composition, homogeneity region is seen from 46 to 52 mol% PbS. PbCuSbS_3 crystallizes in rhombic syngony with parameters of lattice cell: $a = 8.162$; $b = 8.71$; $c = 7.81\text{\AA}$, space group $\text{Pmn}2_1$, $z = 4$. Since the compound PbCuSbS_3 is congruent, it takes part in triangulation of quasiternary system $\text{Cu}_2\text{S} - \text{PbS} - \text{Sb}_2\text{S}_3$. We studied chemical interaction by the systems $\text{Cu}_2\text{S} - \text{PbCuSbS}_3$ and $\text{CuSbS}_2 - \text{Pb}_5\text{Sb}_4\text{S}_{11}$.

Experimental part

For the synthesis we used "high pure" chemical reagents. Rich alloys PbS, Cu_2S were synthesized by visually combined method [2]. Alloys of the system $\text{Cu}_2\text{S} - \text{PbCuSbS}_3$ and $\text{CuSbS}_2 - \text{Pb}_5\text{Sb}_4\text{S}_{11}$ were synthesized and rich alloys were synthesized by ampoule method. Maximum synthesis temperature of alloys is 1350K. After the

end of synthesis with the purpose of achieving equilibrium condition and obtaining homogeneous alloy the samples were annealed at temperature 50 degrees below the temperature of solidus for a month. Annealed alloys were studied by methods of physical-chemical analysis: differential-thermal (DTA), X-ray analysis, as well as micro hardness measurement. Thermograms were recorded on low-frequency thermo-recorder "Thermoscope 2", as a sample we used Al_2O_3 , heating rate is 10^0C/min ; X-ray diffraction analysis was conducted on X-ray diffractometer "D-2 PHASER"; micro hardness was determined on microhardness tester "Thixomet Smart Drive" at loads of each selected phase; microstructure analysis (MSA) of polished etched micro-section was studied on microscope MIM-7. Synthesized alloys are dense; their color varies from black to dark-grey with metallic luster.

Result and discussions

The section $\text{Cu}_2\text{S} - \text{PbCuSbS}_3$. Results of DTA showed that on thermograms of alloys containing up to 40mol% PbCuSbS_3 there are four effects at 350, 600, 935 and 1000-1350K, but on thermograms of alloys containing 40-90 mol% PbCuSbS_3 three endoeffects are observed. Effects conform to phase transformation at 350-600K $\alpha - \text{Cu}_2\text{S} \leftrightarrow \beta - \text{Cu}_2\text{S} \leftrightarrow \gamma - \text{Cu}_2\text{S}$.

For investigation of microstructure of alloys we used etching agents $1\text{NaOH} + 3\%\text{H}_2\text{O}_2$. Data of microstructure analysis showed that near $\alpha - \text{Cu}_2\text{S}$ and quaternary compound PbCuSbS_3 (up to 1 and 3 mol%) alloys consist of one phase, but when increasing the composition of the sec-

ond component two-phase region is observed.

In subsolidus part of the system $\beta + \beta'$ crystallize at the concentration range of 1-46 mol% PbCuSbS_3 . When measuring microhardness of alloys we obtained two rows of values (250-265 and $130-135 \cdot 10^7$ Pa), relating to microhardness of β' (solid solution based on quaternary sulphide PbCuSbS_3) and β (solid solution based on Cu_2S) correspondingly. Results of X-ray diffraction analysis fully conform to DTA and MSA data.

We constructed state diagram of the system $\text{Cu}_2\text{S} - \text{PbCuSbS}_3$ according to research results (fig.1).

As it is seen from the figure liquidus of the system consists of two branches of primary crys-

tallization of phases $\gamma - \text{Cu}_2\text{S}$ and $\beta' - \text{PbCuSbS}_3$, which intersects at double eutectic point.

Coordinates of eutectic point: 40 mol% Cu_2S and 935K.

The section $\text{CuSbS}_2 - \text{Pb}_5\text{Sb}_4\text{S}_{11}$ intersects at three slave systems $\text{CuSbS}_2 - \text{Sb}_2\text{S}_3 - \text{PbCuSbS}_3$, $\text{PbCuSbS}_3 - \text{Sb}_2\text{S}_3 - \text{PbSb}_2\text{S}_4$, $\text{PbSb}_2\text{S}_4 - \text{PbCuSbS}_3 - \text{Pb}_5\text{Sb}_4\text{S}_{11}$. Results of DTA analysis showed that on thermograms of alloys three effects are observed (table 2). Data of microstructure analysis indicates three-phase of alloys. Microhardness measurement values of alloys of the system are given in the table 2.

Table 1

Results of DTA, determination of microhardness of the system $\text{Cu}_2\text{S} - \text{PbCuSbS}_3$

Composition, mol % PbCuSbS_3	Thermal effects of heating, K	Microhardness, $\times 10^7$ Pa
0,0	380, 630, 1390	130
10	350, 600, 935, 1345	135
20	350, 600, 1285	135
30	350, 600, 1210	135
40	350, 600, 1140	135
50	350, 935, 1040	135
55	350, 935, 990	-
60	350, 935	Eutectic
65	350, 935, 970	-
70	350, 935, 990	265
80	350, 935, 1050	265
90	350, 935, 1080	265
95	1010, 1110	265
100	1125	250

Table 2

Results of DTA and microhardness measurement of alloys of the system $\text{CuSbS}_2 - \text{Pb}_5\text{Sb}_4\text{S}_{11}$

Composition, mol% $\text{Pb}_5\text{Sb}_4\text{S}_{11}$	Thermal effects of heating, K	Microhardness, $\times 10^7$ Pa
5	600, 790, 825	230, 180, 250
10	600, 740, 823	230, 180, 250
20	600, 680, 800	230, 180, 250
30	600, 625, 775	230, 180, 250
40	600, 740, 790	230, 180, 250
50	600, 700, 900	230, 180, 250
56	675, 920	250, 124
60	625, 650	180, 124, 250
65	625, 750, 900	180, 124, 250
70	800, 925	250, 180
72	700, 795	250, 124, 210
80	700, 720, 875	250, 124, 210
90	700, 850, 925	250, 124, 210
100	1073	210

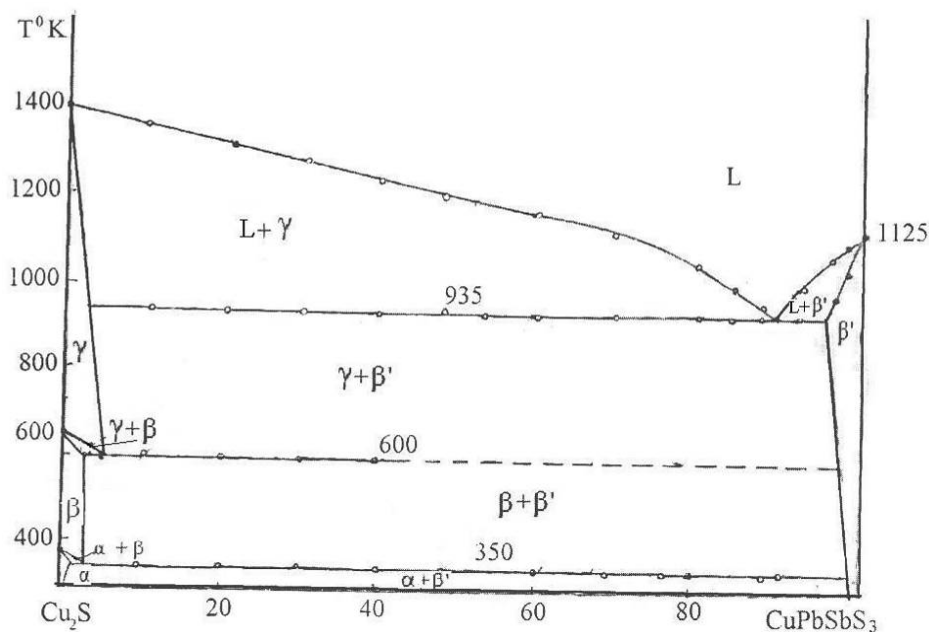


Fig. 1. State diagram of the system $\text{Cu}_2\text{S} - \text{PbCuSbS}_3$

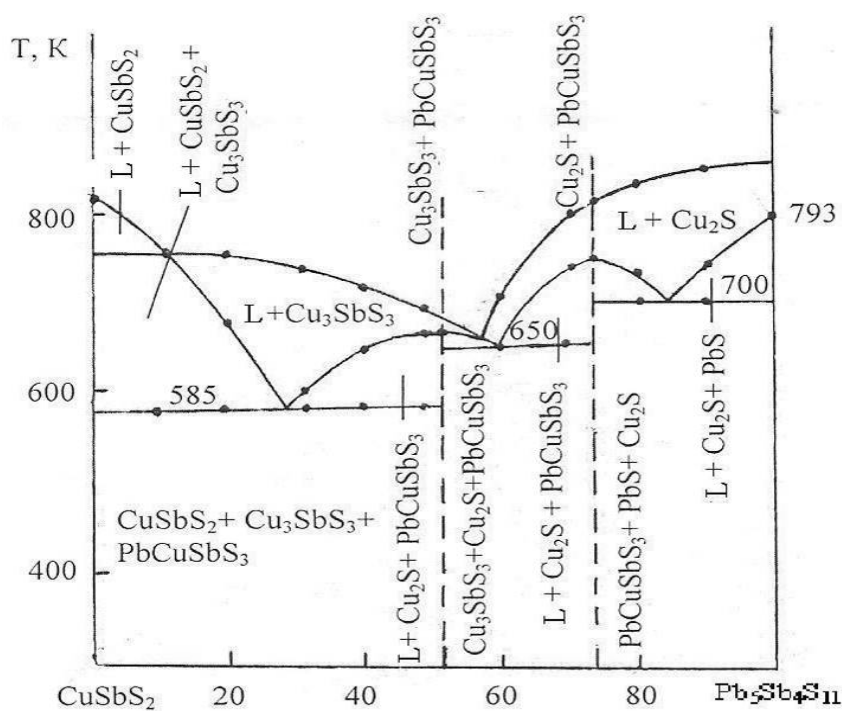
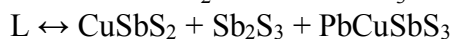
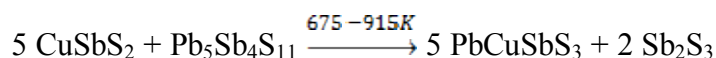


Fig. 2. State diagram of the section $\text{CuSbS}_2 - \text{Pb}_5\text{Sb}_4\text{S}_{11}$

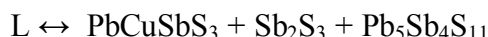
According to the results of researches state diagram of the system $\text{CuSbS}_2 - \text{Pb}_5\text{Sb}_4\text{S}_{11}$ was constructed (fig. 2). At interval of concentrations 0-56 mol% $\text{Pb}_5\text{Sb}_4\text{S}_{11}$ section intersects at secondary ternary system $\text{CuSbS}_2 - \text{Sb}_2\text{S}_3 - \text{PbCuSbS}_3$. Liquidus of this part of the section consists of branches of primary crystallization of CuSbS_2 and PbCuSbS_3 . Alloys finally solidify at 600K.



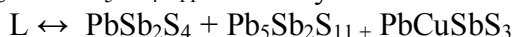
The composition 56 mol% $\text{Pb}_5\text{Sb}_4\text{S}_{11}$ answers to intersection point of section $\text{CuSbS}_2 - \text{Pb}_5\text{Sb}_4\text{S}_{11}$ with quasibinary section $\text{PbCuSbS}_3 - \text{Sb}_2\text{S}_3$ in which the reaction proceeds:



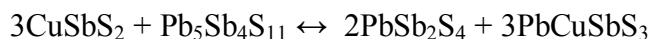
The part of section (50 – 70 mol% $\text{Pb}_5\text{Sb}_4\text{S}_{11}$) intersects at the slave triangle $\text{PbCuSbS}_3 - \text{Sb}_2\text{S}_3 - \text{PbSb}_2\text{S}_4$. In this secondary system only eutectic transformations are observed. Crystallization of alloys ends at the temperature of ternary eutectic 620K:



Finally the part of section (70 – 100 mol% $\text{Pb}_5\text{Sb}_4\text{S}_{11}$) intersects at the secondary triangle $\text{PbSb}_2\text{S}_4 - \text{PbCuSbS}_3 - \text{Pb}_5\text{Sb}_4\text{S}_{11}$. In this sub-system liquidus consists of two branches conforming to crystallization of PbCuSbS_3 and $\text{Pb}_5\text{Sb}_4\text{S}_{11}$. Final crystallization is over at 700K



The composition 70 mol% $\text{Pb}_5\text{Sb}_4\text{S}_{11}$ is intersection point of section with quasibinary cross-section $\text{PbSb}_2\text{S}_4 - \text{PbCuSbS}_3$ where the reaction proceeds:



According to the results we constructed state diagram of the system $\text{CuSbS}_2 - \text{Pb}_5\text{Sb}_4\text{S}_{11}$ (fig.2).

By this way we studied two sections by quasiternary system $\text{Cu}_2\text{S} - \text{Sb}_2\text{S}_3 - \text{PbS}$ and established that the section $\text{Cu}_2\text{S} - \text{PbCuSbS}_3$ is quasibinary, but $\text{CuSbS}_2 - \text{Pb}_5\text{Sb}_4\text{S}_{11}$ is nonquasibinary.

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*Institute of Catalysis and Inorganic Chemistry
of ANAS
chem.@science.az*

$\text{Cu}_2\text{S} - \text{PbCuSbS}_3$ və $\text{CuSbS}_2 - \text{Pb}_5\text{Sb}_4\text{S}_{11}$ SİSTEMLƏRİNDƏ FAZA TARAZLIĞI

Ö.M.Əliyev, D.S.Əjdərova, T.F.Maqsudova, V.M.Rəhimova, T.A.Səlimova

Fiziki-kimyəvi analiz metodları ilə $\text{Cu}_2\text{S} - \text{PbCuSbS}_3$ və $\text{CuSbS}_2 - \text{Pb}_5\text{Sb}_4\text{S}_{11}$ sistemləri tədqiq olunmuşdur. Müəyyən edilmişdir ki, $\text{Cu}_2\text{S} - \text{PbCuSbS}_3$ kəsiyi $\text{Cu}_2\text{S} - \text{PbS} - \text{Sb}_2\text{S}_3$ üçlü sisteminin kvazibinar, $\text{CuSbS}_2 - \text{Pb}_5\text{Sb}_4\text{S}_{11}$ isə qeyri-kvazibinar kəsiyidir.

Açar sözlər: evtektika, kvazibinar, bərk məhlul

ФАЗОВОЕ РАВНОВЕСИЕ В СИСТЕМАХ $\text{Cu}_2\text{S} - \text{PbCuSbS}_3$ и $\text{CuSbS}_2 - \text{Pb}_5\text{Sb}_4\text{S}_{11}$

О.М.Алиев, Д.С.Аждарова, Т.Ф.Максудова, В.М.Рагимова, Т.А.Салимова

Система PbCuSbS_3 является квазибинарной, эвтектической (40 мол % Cu_2S , 995K), а $\text{CuSbS}_2 - \text{Pb}_5\text{Sb}_4\text{S}_{11}$ неквазибинарным сечением квазитройной системы $\text{Cu}_2\text{S} - \text{PbS} - \text{Sb}_2\text{S}_3$. Методами физико-химического анализа (ДТА, РФА, МСА, а также измерением микротвердости) исследованы фазовые равновесия в системах $\text{Cu}_2\text{S} - \text{PbCuSbS}_3$ и $\text{CuSbS}_2 - \text{Pb}_5\text{Sb}_4\text{S}_{11}$. Построены Т-х диаграммы состояния.

Ключевые слова: эвтектика, квазибинарный, твердый раствор