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Study of quasi-ternary system Cu_2S-SnS_2-Sb_2S_3 by section Cu_2SnS_3-$CuSbS_2$

Chemistry and chemical technology

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For the first time phase equilibria in quasi-ternary system Cu_2S-SnS_2-Sb_2S_3 by sections Cu_2SnS_3-$CuSbS_2$ were studied using the methods of differential-thermal, X-ray phase, microstructure analyses, as well as measurement of micro hardness and density. It was established, that the system Cu_2SnS_3-$CuSbS_2$ is quasi-binary section of eutectic type and its state diagram was constructed. Coordinates of eutectics correspond to 10 mol% Cu_2SnS_3 and temperature 760 K. Solid solution ranges in sections were determined according to primary components. Solid solution ranges based on Cu_2SnS_3 (4 mol% $CuSbS_2$) and $CuSbS_2$ (3 mol% Cu_2SnS_3) were detected at room temperature (300K).

Key words: eutectic, Cu_2SnS_3, quasi-binary, $CuSbS_2$, ternary system, solid solution.

Introduction

One of the rapid developing directions in searching new efficient semiconductor materials is creation of ternary or quaternary semiconductors. Semiconductors with a layer structure, such as Cu_2S, SnS_2 and Sb_2S_3, the components of the studied system are of special interest. Interest in phases with a layer structure is due to the use of lamellar semiconductors in optoelectronics and their specific physical and chemical properties [1].

V_2VI_3 group semiconductors attract attention of researchers thanks to unique properties in term of applications [2–9]. In particular, phases based on Sb_2S_3 attract interest for their applicability in microwave, switching and electronic devices in optics. Cu_2SnS_3 compound, which belongs to a class of ternary diamond-like semiconductors, is a perspective material for using in optoacoustics, in non-linear optical devices and photo-electric elements [10-12].

Statement of the problem

Literary data on phase diagram of ternary system Cu_2S-SnS_2-Sb_2S_3 are not available. Compounds Cu_2S, SnS_2, Sb_2S_3 and boundary quasi-binary systems Cu_2S-SnS_2, SnS_2-Sb_2S_3-Cu_2S-Sb_2S_3 of ternary system Cu_2S-SnS_2-Sb_2S_3 were studied in detail in literature.

According to the data [13], three compounds are formed in the system Cu_2S-SnS_2: Cu_4SnS_4 is crystallized in rhombic syngony, lattice cell parameters are a=13.558, b=7.681, c=6.412 Å space group Pnma [14]. Cu_2SnS_3 melts congruently at 1127 K [11, 12] and is crystallized in monocline structure space group Cc; a=6,653, b=15,87, c=6, 665 Å, $\beta=109^0$, Z=4 [15]. $Cu_2Sn_4S_9$ is crystallized in cubic structure, a=10.40 Å [16]. Cu_2S-SnS_2 system was also investigated in works [17-19] and only one of the above-stated Cu_2SnS_3 compounds was detected. In [20, 21] various values of melting point are given for Cu_2SnS_3. Authors [16] determined that four ternary compounds are formed in Cu_2S-SnS_2 system. Cu_2SnS_3 melts congruently at 1123K [16]. The rest three compounds have structures of $Cu_4Sn_3S_6$, Cu_4SnS_4, $Cu_2Sn_4S_9$, melt incongruently at 1063, 1083 and 938K, respectively.

In works [22, 23] quasi-binary system Cu_2S-Sb_2S_3 was investigated using the methods of X-ray phase and differential-thermal analyses and formation of two $CuSbS_2$ and Cu_3SbS_3 intermediate compounds was found out. According to the works [24, 25], quasi-binary section Cu_2S-Sb_2S_3 is characterized by formation of only one congruently melting compound $CuSbS_2$ at 825K. Works [26-29] confirmed the presence of compounds Cu_3SbS_3 and $CuSbS_2$ in Cu_2S-Sb_2S_3 system. In work [28] the detailed phase diagram of Cu2S-Sb2S3 system is presented. $CuSbS_2$ has a rhombic syngony with lattice parameters: space group Pbnm; a=14.465, b=6,008, c=3,784 Å, Z=4 or a=6.00, b=3.78, c=14.14 Å [30, 31]. Authors of the work [30] showed, that temperature of polymorphic transformation of Cu_3SbS_3 equals to 632K. High-temperature modification has a rhombic syngony a= 7.81, b= 10.25, c= 6.60A^0 and low-temperature cubic syngony a=10.24A^0. Cu_2S-Sb_2S_3 system was also investigated in works [32-34]. Three compounds Cu_3SbS_3, $Cu_{10}Sb_4S_{11}$ and $CuSbS_2$ were found. Results of these works practically coincide with the data [28], in which it was also shown that Cu_3SbS_3 melts with maximum at 885K [28].

SnS_2-Sb_2S_3 system was studied in the work [35]. It was found that the section is quasi-binary section of ternary Sn-Sb-S system. The compound of $SnSb_2S_5$, which melts incongruently at 735K was found in the system.

The aim of our study is to define phase diagram of quasi-binary section Cu_2SnS_3-$CuSbS_2$ of the system Cu_2S-SnS_2-Sb_2S_3.

Solution of the problem

Primary sulfides ($CuSbS_2$ and Cu_2SnS_3) from high-purity elements were synthesized in quartz ampoules, vacuumed up to 0.133 Pa. Quaternary alloys of Cu_2SnS_3-$CuSbS_2$ systems were synthesized from alloying compositions at 850-1150 K depending on composition. Annealing was performed at 50-60K lower than a solidus within 240 hours for homogenization of alloys.

Interaction in Cu_2SnS_3-$CuSbS_2$ systems was studied using the methods of differential-thermal (DTA), X-ray phase, microstructural (MSA) analyses and measurement of micro hardness and gravity test. X-ray phase analysis was performed on D 2 PHASER using CuKα-radiation Ni-filter.

Differential-thermal analysis of alloys was carried out on NTR-73 device with heating rate of 10 grade/min. Calibration chrome-aluminum thermocouple was used, Al_2O_3 served as standard. We used etching agent NH_4NO_3(3-8 weight.%) + $K_2Cr_2O_7$(0,02-0,5 weight.%) + cons. H_2SO_4 to study microstructure of alloys, etching time – 20 sec. Micro hardness of alloys was measured on PMT-3 micro hardness tester at loads 0,01 and 0,02H. MSA of alloys of systems was investigated on metallographic microscope MIM-8 on previously etched microsections polished with GOI paste.

Phase diagram of system Cu_2SnS_3-$CuSbS_2$ is determined by methods of physical and chemical analysis (DTA, MSA, X-ray phase, measurement of micro hardness and density) using thermodynamic calculations.

13 samples with various compositions were synthesized to study phase equilibrium in section Cu_2SnS_3-$CuSbS_2$. According to DTA, X-ray phase and MSA data, we constructed phase diagram of system Cu_2SnS_3-$CuSbS_2$ (Figure).

As figure shows system Cu_2SnS_3-$CuSbS_2$ is quasi-binary and belongs to eutectic type and results in formation of solid solutions on the basis of Cu_2SnS_3 и $CuSbS_2$. Coordinates of eutectic point are 10 mol% Cu_2SnS_3 and 760K. DTA results show that interaction between Cu_2SnS_3 and $CuSbS_2$ is not complex.

X-ray phase results of alloys of this system are coordinated with DTA data and confirm the existence of solid solutions on the basis of Cu_2SnS_3 and $CuSbS_2$. It is established that, diffraction lines of alloys comprising 0-3mol $CuSbS_2$ are identical with diffractogram of Cu_2SnS_3. They are solid solutions based on Cu_2SnS_3. Diffraction lines of alloys of 3-96 mol% Cu_2SnS_3 consist of reflection lines of α($CuSbS_2$) and β(Cu_2SnS_3) phases. Alloys of compositions 0-4 mol% Cu_2SnS_3

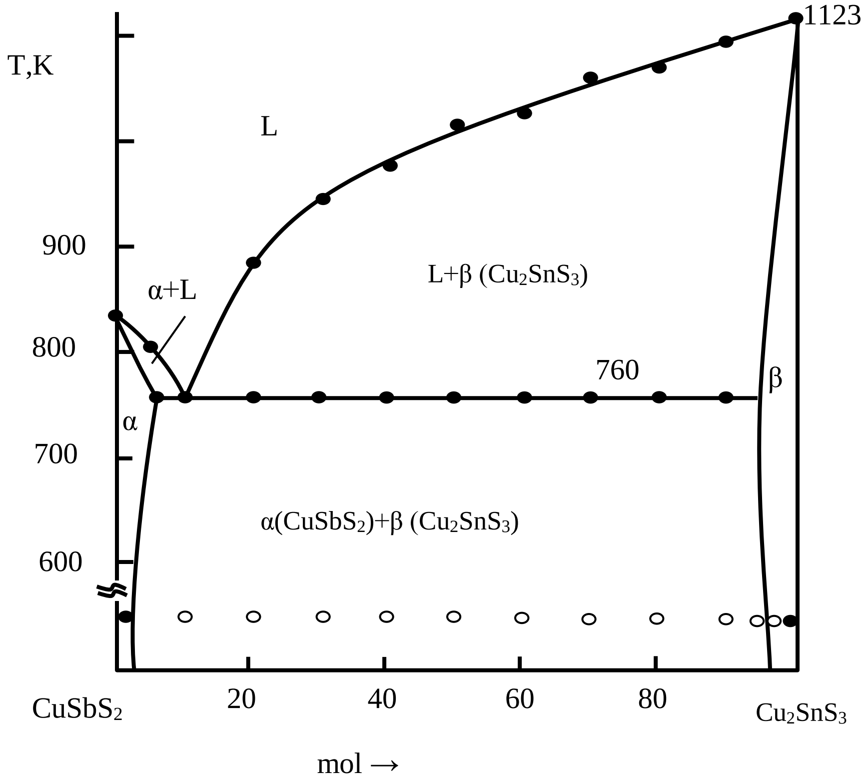

Figure. Phase diagram of system $CuSbS_2$-Cu_2SnS_3

have diffractograms identical to diffractogram of $CuSbS_2$ and are solid solutions based on $CuSbS_2$. Alloys with 99, 98, 97, 96, 94, 93 mol % on both sides were synthesized additionally to determine borders of solid solutions. These alloys were annealed for 320 hours at 750, 500 K and then tempered. After heat treatment and studying microstructure of these alloys solubility borders were defined.

The study of microstructure showed that, alloys with compositions of 0-4 mol% and 97-100 mol % $CuSbS_2$ are single-phase. Alloys with of 3-96 mol% Cu_2SnS_3 are two-phase.

Solid solutions based on $CuSbS_2$ are crystallized in rhombic syngony, and solid solutions based on Cu_2SnS_3 are crystallized in monoclinic syngony (Table 1).

Table 1. Crystal cell parameters of solid solutions in system Cu_2SnS_3-$CuSbS_2$

Composition mol % $CuSbS_2$	Syngony	Space group	Cell parameters, A^0
100	Rhombic	Pbnm	a=14.65; b=6.008; c=3.784
99	Rhombic	Pbnm	a=14.63; b=6.007; c=3.782
98	Rhombic	Pbnm	a=14.61; b=6.005; c= 3.779
97	Rhombic	Pbnm	a=14.59; b=6.001; c=3.777
4	Monoclinic	Cc	a=6.671; b=11.595; c=6.77
3	Monoclinic	Cc	a=6.669; b=11.593; c=.6.74
2	Monoclinic	Cc	a=6.667; b=11.591; c=6.71
1	Monoclinic	Cc	a=6.665; b=11.589; c=6.68
0	Monoclinic	Cc	a=6.653; b=11.587; c=6.65

A technique was developed and technological conditions were selected to grow monocrystals of solid solutions based on $CuSbS_2$ using Bridgman- Stockbarger method. Polycrystalline alloys in the amount of 7 g were synthesized for growth of monocrystals, and then they were crushed and placed into an ampoule, the last was evacuated and placed into two temperature furnaces with predefined temperature difference. The furnace was moved at 3 mm/hour, whereas the ampoule remained motionless. Such design allows eliminating disturbances when ampoule is shaken. As a result of numerous experiences zone temperatures of furnaces and furnace movement were detected. Qualitative monocrystals were grown using a developed technique. Table 2 shows the mode of producing monocrystals according to a number of experiments. The technology of growing monocrystals of solid solutions based on Cu_2SnS_3 was developed using the method of chemical gas-transport reaction.

Table 2. Optimum mode for the growth of single-crystals of solid solutions based on $CuSbS_2$

Composition	T, K	Mass of single-crystals, g
$(CuSbS_2)_{0,999}(Cu_2SnS_3)_{0,001}$	750-800	7,3
$(CuSbS_2)_{0,998}(Cu_2SnS_3)_{0,002}$	750-800	7,5
$(CuSbS_2)_{0,997}(Cu_2SnS_3)_{0,003}$	750-800	7,8

Quantity of substance 4–5 g, concentration of conveyor (iodine) is 5 mg. Experiments showed that smaller concentrations of iodine are ineffective, but larger concentrations increase the rate. Table. 3 shows an optimum temperature mode of single-crystal growth of solid solutions based on Cu_2SnS_3. Single -crystals of solid solutions were grown at the following mode: temperature of a hot zone - 1050 K, cold zone - 950 K.

Table 3. Optimum mode for the growth of single-crystals of solid solutions based on Cu_2SnS_3

Composition	Temperature, K		Concentration of iodine, mg/cm^3	Growth time, hr	Size of single-crystals, mm^3
	T_1	T_2			
$(Cu_2SnS_3)_{0,999}$ $(CuSbS_2)_{0,001}$	1050	950	5	72	1.0×1.0×0.5
$(Cu_2SnS_3)_{0,998}$ $(CuSbS_2)_{0,002}$	1050	950	5	72	1.0×1.0×0.5
$(Cu_2SnS_3)_{0,997}$ $(CuSbS_2)_{0,003}$	1050	950	5	72	1.0×1.0×0.5

Conclusion

1. State diagram in a wide range of concentrations of section Cu_2SnS_3-$CuSbS_2$ was constructed for the first time and it was found that it is quasi-binary section of quasi-ternary system Cu_2S-SnS_2-Sb_2S_3.
2. It was established that, section Cu_2SnS_3-$CuSbS_2$ is of eutectic type, coordinate of the eutectic point corresponds to 10 mol% Cu_2SnS_3 and 760K.
3. Solid solution ranges based on Cu_2SnS_3-$CuSbS_2$ are defined. Solid solutions based on Cu_2SnS_3 at room temperature (300K) are formed up to 4 mol%, but on the basis of $CuSbS_2$ it is found to 3mol%.
4. Single-crystals of solid solutions based on Cu_2SnS_3 were grown using the method of chemical transport reactions, but single-crystals based on $CuSbS_2$ were grown using Bridgman-Stockbarger method.
5. It was determined that solid solutions on the basis of $CuSbS_2$ are crystallized in monoclinic syngony, solid solutions based on Cu_2SnS_3 are crystallized in rhombic syngony.

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Xülasə

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Cu_2S-SnS_2-Sb_2S_3 kvaziüçlü sistemində Cu_2SnS_3-$CuSbS_2$ kəsiyinin tədqiqi

İlk dəfə differensial termiki, rentgenfaza, mikrostruktur, mikrobərkliyin ölçülməsi və sıxlığın təyini kimi bir sıra fiziki-kimyəvi analız üsullarından istifadə etməklə Cu_2SnS_3-$CuSbS_2$ kəsiyində faza tarazlığı öyrənilmişdir. Kəsiyin hal diaqramı qurulmuş və müəyyən olunmuşdur ki, Cu_2SnS_3-$CuSbS_2$ kəsiyi Cu_2S-SnS_2-Sb_2S_3 kvaziüçlü sistemin kvazibinar kəsiyidir. Tədqiq olunan kəsikdə otaq temperaturunda Cu_2SnS_3 əsasında 4 mol% ($CuSbS_2$),$CuSbS_2$ əsasında isə 3 mol% (Cu_2SnS_3) bərk məhlul sahəsi yaranır. Cu_2SnS_3-$CuSbS_2$ kəsiyində alınan evtektik nöqtələrin koordinatı isə 10 mol% Cu_2SnS_3 və 760К təşkil edir.

Açar sözlər: evtektika, Cu_2SnS_3, kvazibinar, $CuSbS_2$, üçlü sistem, bərk məhlul.

Резюме

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Исследование квазитройной системы Cu_2S-SnS_2-Sb_2S_3 по разрезу Cu_2SnS_3-$CuSbS_2$

Впервые с помощью методов дифференциально-термического, рентгенофазового, микроструктурного анализа, а также измерением микротвердости и плотности изучены фазовые равновесия в квазитройной системе Cu_2S-SnS_2-Sb_2S_3 по сечениям Cu_2SnS_3-$CuSbS_2$. Установлено, что система Cu_2SnS_3-$CuSbS_2$ является квазибинарным разрезом эвтектического типа и построена ее диаграмма состояния. Координаты эвтектики соответствуют 10 мол% Cu_2SnS_3 и температуре 760 К. На основе исходных компонентов в разрезе были определены области твердых растворов.

Ключевые слова: эвтектика, Cu_2SnS_3, квазибинар, $CuSbS_2$, тройная система, твердый раствор.