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REFINEMENT OF PHASE DIAGRAM IN THE Cu_2S-GeS_2 SYSTEM

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Abstract: *Given the inconsistency of the data available in the literature, the Cu_2S-GeS_2 system was re-studied through the use of DTA and XRD methods. A special emphasis is laid on obtaining equilibrium alloys and preventing deviations of their composition from the stoichiometry of this section. The constructed phase diagram reflects the presence of the two ternary compounds in the system: Cu_8GeS_6 and Cu_2GeS_3. The first melts incongruently at 1253 K and has the phase transition at 328 K, and the second melts congruently at 1215 K.*
Keywords: *Cu-Ge-S system, phase diagram, copper tiogermanates, Cu_8GeS_6, Cu_2GeS_3, eutectic.*
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Introduction

Complex copper chalcogenides are valuable functional materials with thermoelectric, photoelectric, optical, and other properties [1-8]. Recent years marked growth of interest in environmentally friendly thermoelectric materials based on these compounds [1, 9-12]. In addition, many complex copper chalcogenides have mixed ionic-electronic conductivity which makes them very promising for use in the development of photoelectrode materials, electrochemical converters of solar energy, ion-selective sensors, photo-electrochemical visualizers, ionizers, etc. [1, 13-18].

The development of methods for directed synthesis of new complex chalcogenide phases is based on phase equilibriums and thermodynamic data for the corresponding systems [19-22]. Complexes of similar data for a number of complex chalcogenide systems were obtained in [23–32].

It should be noted that Cu-Ge-S system is characterized by the formation of ternary compounds with interesting physical properties [1, 8, 12, 13, 15-17] to be used in practice. In spite of the fact that phase equilibriums in the Cu-Ge-S system and particularly, in the quasibinary section Cu_2S-GeS_2 were studied in a number of works [5, 33-35], there are some contradictions in the results obtained.

According to [33], this system is characterized by the formation of two ternary compounds Cu_8GeS_6 and Cu_2GeS_3, melting incongruently at 1253 and 1213 K, respectively. According to the data of [34], only the Cu_2GeS_3 compound is formed in the system which melts congruently at 1229 K. In [**5**], it showed that the Cu_2GeS_3 melts congruently at 1215 K. The data of [33-35] significantly differ from each other in the coordinates of invariant points. In addition, when studying the $2Cu_2S + GeSe_2 \leftrightarrow 2Cu_2Se + GeS_2$ mutual system [24], we observed some discrepancy between our experimental data and the patterns of phase equilibriums along the Cu_2S-GeS_2 section.

In view of the foregoing, the objective of this work is to reinvestigate phase equilibriums in the Cu_2S-GeS_2 system.

Experimental part

To study the Cu_2S-GeS_2 system, first initial binary compounds (each 20 g) were synthesized. The syntheses were carried out by direct interaction of elementary components of a high degree of purity in evacuated (~10^{-2}Pa) quartz ampoules in a dual-zone inclined furnace. The lower "hot" zone was heated up to 1200 K, and the upper "cold" up to 650 K (boiling point of sulfur - 718 K [**35**]). In this temperature regime, sulfur completely interacts for two hours with metallic copper, as evidenced by the absence of traces of sulfur (dark brown vapor phase and droplets) on inner walls of the ampoule. Then, to obtain a stoichiometric composition in line with the recommendation [24], the ampoule was sharply cooled in ice water.

Synthesis of the Cu_2S was carried out in a similar way. Elementary germanium and sulfur were powdered, transferred into an ampoule which was pumped out and sealed. The temperature of the "hot" zone was raised up to 800 K, and the "cold" to 650 K. Note that in terms of this temperature mode, most of the sulfur was absorbed by germanium in 25-30 hours. After this, the ampoule was completely transferred to the "hot" zone and kept at 800 K for another 10 hours and then chilled.

Both synthesized compounds were identified by DTA and XRD.

Alloys of the Cu_2S-GeS_2 system (each 0.5 g) were prepared by melting starting compounds in various ratios inside evacuated thick-walled quartz ampoules. The temperature was slowly (over 5 hours) heated up to 1000 K, kept for 10 hours, and then heated up to 1300 K (0-50 mol%) and 1200 K (55-95 mol%). After melting, the temperature was lowered to 800 K where thermal annealing was performed for 500 hours.

All prepared samples were analyzed by means of DTA, XRD, and EMF technique. The XRD data were collected at room temperature using a Bruker D8 ADVANCE diffractometer (with Cu-Kα_1 radiation). DTA of the equilibrated alloys was carried out by means of NETZSCH 404 F1 Pegasus system device. The heating rate was 10 K/min.

Results and discussion

Analysis of powder X-ray diffraction patterns of annealed and slowly cooled alloys with selective compositions showed the presence of two Cu_8GeS_6 and Cu_2GeS_3 ternary compounds with practically constant compositions. X-ray diffraction patterns of alloys with intermediate compositions consisted of sets of reflection lines with two phases to confirm the presence of two-phase mixtures, Cu_2S- Cu_8GeS_6, Cu_8GeS_6-Cu_2GeS_3, and Cu_8GeS_6+GeS_2. Cited as an example, Fig. 1 shows powder diffraction patterns of Cu_8GeS_6, Cu_2GeS_3 compounds and an alloy with composition 30 mol% GeS_2. As you can see, this alloy is a two-phase mixture of these ternary compounds. The diffraction pattern does not contain reflection lines that could be attributed to Cu_4GeS_4 or another phase.

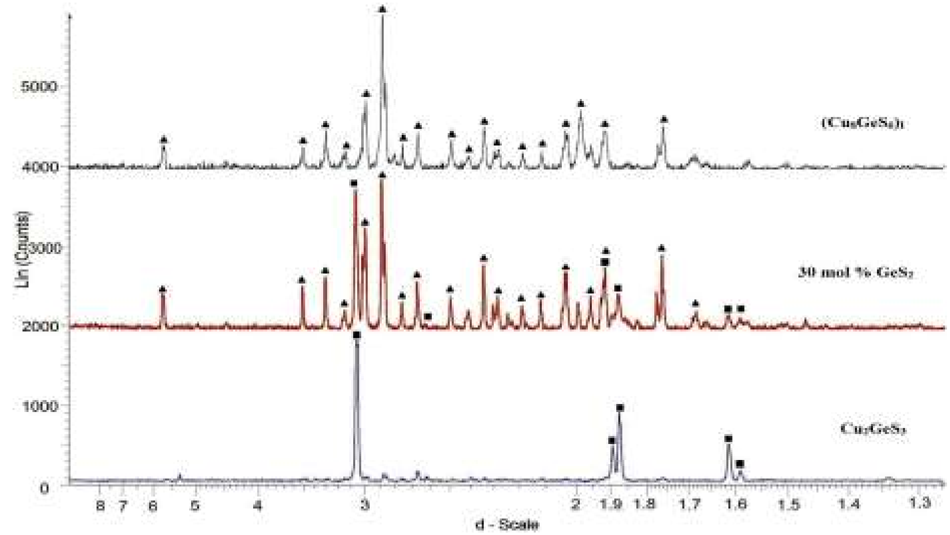

Fig.1. Powder diffraction patterns Cu_8GeS_6, Cu_2GeS_3 compounds and alloy with composition of 30 mol% GeS_2

The DTA data are given in the Table, and the diagram based thereon is shown in Fig. 2. As can be seen, two ternary compounds are formed in the system: Cu_8GeS_6 and Cu_2GeS_3. The first melts by peritectic decomposition at 1253 K and undergoes a polymorphic transformation at 328 K, while the second melts congruently at 1215 K. The peritectic point (P) has a composition of 25 mol%. There are two eutectics (e_1 and e_2) in the system that have compositions of 43 and 90 mol% and are crystallized at 1205 K and 1092 K, respectively. The horizontal lines at 375 and 328 K correspond to polymorphic transitions of Cu_2S and Cu_8GeS_6, respectively.

Table 1. DTA data for the Cu_2S-GeS_2 alloys

Composition, mol % GeS_2	**Thermal effects, K**	
	Isothermal	**Polythermal**
Cu_2S	377; 1403	-
5	375; 1255	1255-1385
10	328; 375; 1252	1252-1330
20	328; 1253	1253-1285
25	330; 1250	1208-1250
30	328; 1205	1205-1247
40	326; 1205	1205-1222
45	1205	-
50	1215	-
52	1090	1090-1212
60	1090	1090-1206
70	1095	1095-1185
80	1092	1092-1165
90	1092	-
95	1090	1090-1113
100	1120	-

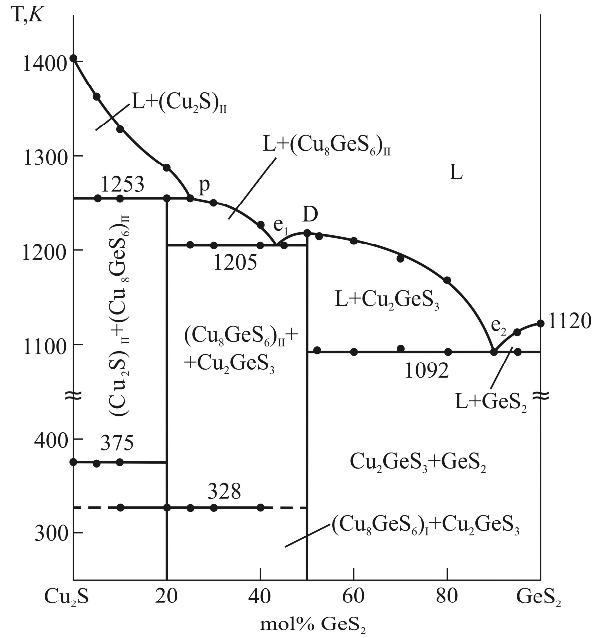

Fig.2. Phase diagram of the Cu_2S-GeS_2 system

Comparison of the constructed phase diagram with the literature data [5, 33-34] shows that in many respects it is in accord with [33]. The main difference concerns the melting character of Cu_2GeS_3. According to our data, this compound melts congruently and forms an eutectic with Cu_8GeS_6, whereas according to [33], the horizontal at 1213 K extends to 70 mol% GeS_2 and corresponds to peritectic equilibrium. According to Fig. 2, this horizontal corresponds to a temperature of 1205 K and refers to eutectic equilibrium. We have not confirmed the existence of ternary compounds of the compositions Cu4GeS4 and Cu2Ge2S5 indicated in [5, 36]. Perhaps they are metastable phases and are absent in the equilibrium phase diagram.

Conclusion

Cu_2S-GeS_2 system was examined in detail by DTA and XRD methods and phase diagram was constructed. Two ternary Cu_8GeS_6 and Cu_2GeS_3 compounds were found in the system. Cu_8GeS_6 melts incongruently at 1253 K and has a phase transition at 328 K while Cu_2GeS_3 melts congruently at 1215 K.

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Cu_2S-GeS_2 SİSTEMİNİN FAZA DİAQRAMININ DƏQİQLƏŞDİRİLMƏSİ

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Cu_2S-GeS_2 sisteminə aid ədəbiyyat məlumatlarının ziddiyyətli olmasını nəzərə alaraq, bu sistemdə faza tarazlıqları DTA və RFA üsulları ilə təkrar tədqiq edilmişdir. Tədqiqatlar zamanı nümunələrin tarazlıq halına gətirilməsinə və onların tərkiblərinin baxılan sistemin T-x müstəvisi üzərində olmasına xüsusi diqqət verilmişdir. Qurulmuş faza diaqramına əsasən, sistemdə 2 üçlü birləşmə mövcuddur: Cu_8GeS_6 və Cu_2GeS_3. Birinci 1253 K-də inkonqruent əriyir və 328 K-də polimorf çevrilməyə məruz qalır, ikinci isə 1215 K-də konqruent əriyir.
Açar sözlər: *Cu-Ge-S sistemi, faza diaqramı, mis-tiogermanatları, Cu_8GeS_6, Cu_2GeS_3, evtektika.*

УТОЧНЕНИЕ ФАЗОВОЙ ДИАГРАММЫ СИСТЕМЫ Cu_2S-GeS_2

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Учитывая противоречивость имеющихся в литературе данных, в работе методами ДТА и РФА повторно изучена система Cu_2S-GeS_2. Особое внимание уделено получению равновесных сплавов и предотвращению отклонения их состава от стехиометрии данного разреза. Построенная фазовая диаграмма отражает наличие в системе двух тройных соединений: Cu_8GeS_6 и Cu_2GeS_3. Первое плавится инконгруэнтно при 1253 К и имеет фазовый переход при 328 К, а второе плавится конгруэнтно при 1215 К.
Ключевые слова: *система Cu-Ge-S, фазовая диаграмма, тиогерманаты меди, Cu_8GeS_6 и Cu_2GeS_3, эвтектика.*