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CHEMICAL INTERACTION AND GLASS FORMATION IN THE As_2S_3-$CuCr_2Te_4$ SYSTEM

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The character of the chemical interaction and glass formation in the As_2S_3-$CuCr_2Te_4$ system was explored by means of physicochemical analysis (DTA, MSA, XRD, density and microhardness measurements) and a phase diagram was constructed. It was established that the state diagram of the system is a quasi-binary eutectic type. In the system narrow homogeneous regions of up to 1.5 mol % As_2S_3 and 3.5% mol % $CuCr_2Te_4$ were detected. Compounds As_2S_3 and $CuCr_2Te_4$ with each other form a eutectic composition of 10 mol. % $CuCr_2Te_4$ with a melting point of 270^{o}C. Under ordinary conditions, in the As_2S_3-$CuCr_2Te_4$ system based on As_2S_3, the glass-forming region reaches 15 mol % $CuCr_2Te_4$.

Keywords: *eutectic, glass formation, density, microhardness, syngony.*
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Introduction

The glassy chalcogenides As_2S_3 and As_2Se_3 and alloys doped with some chalcogenides as photosensitive and magneto-optical materials have attracted the attention of researchers in recent years [1-8]. In this regard, multicomponent systems with the participation of arsenic sulfide and selenide are intensively studied [9-11]. Chromium chalcogenides and the obtained ternary compounds based on it have magnetic properties [12-14]. Therefore, the study into interaction between As_2Se_3 and $CuCr_2Te_4$ compounds is very important.

The aim of this work is to study chemical interactions and glass formation in the As_2S_3-$CuCr_2Te_4$ system and build a phase diagram.

The glassy compound As_2S_3 melts with open maximum at 310°C and crystallizes in monoclinic syngony with lattice parameters as follows: a = 11.49; b = 9.59; c = 4.25 Å, β = 90^{o}27$^/$, sp.gr. P 21/n [15]. The density and microhardness of the glassy As_2S_3 compound are respectively ρ = 3.187 g/cm^3 and Hμ = 128-145 MPa.

The initial compound $CuCr_2Te_4$ melts congruently at 1155°C [14] and crystallizes in a cubic syngony with lattice parameters a = 11.134 Å, sp.gr. Fd-3m, density ρ = 6.51 g/cm^3 [16].

Experimental part

The alloys were annealed at 270°C for 350 hours. Alloys of the system were obtained from ligatures As2S3 and CuCr2Te4, previously synthesized from elements in quartz ampoules pumped out to 0.133 Pa in the range of temperature 600-1200^{o}C depending on the alloy composition. The alloys were annealed at 270°C for 350 hours.

The alloys of the As_2S_3-$CuCr_2Te_4$ system were studied by differential thermal (DTA), X-ray diffraction (XRD), microstructural (MSA) analysis, as well as microhardness measurements and density determination.

Thermal analysis of the alloys was carried out on a TERMOSKAN-2 instrument with accuracy of 3-5°C, whiht chromel-alumel thermocouple. The heating rate is 5 deg/min. X-ray phase analysis was performed on an X-ray device of D2 PHASER model using CuKα radiation and a Ni filter. Microstructural analysis of alloys of the As2S3-CuCr2Te4 system was carried out by means of a MIM-8 microscope. The microhardness of the phases was measured on a PMT-3 instrument with accuracy of 5% while the density of the samples was determined by the pycnometric method.

Results and its discussion

Alloys of the As_2S_3-$CuCr_2Te_4$ system with high As_2S_3 content are bright red, brittle layered, and with the $CuCr_2Te_4$ increased content; the samples acquire a dark brown hue. Alloys rich in As_2S_3 are obtained by a glassy appearance. They are resistant to air and water. Concentrated mineral acids (HNO_3, H_2SO_4) and alkalis (NaOH, KOH) decompose them. In order to crystallize glassy alloys, 0-25 mol % of As_2S_3–based $CuCr_2Te_4$ was annealed at 170° C for 600 hours while the remaining alloys were annealed at 300°C for 240 hours. A physicochemical study was performed before and after annealing. Some physicochemical properties of alloys from the glass region are given in Table 1.

Table 1. Some physicochemical properties of glasses of the As_2S_3-$CuCr_2Te_4$ system

Composition, mol %		Thermal effects, °C			Microhardness, MPa	Density q/cm^3	Results MSA
As_2S_3	$CuCr_2Te_4$	Tg	Ткр.	Тпл.			
100	0	170	230	310	1350	3,20	Glass,
97	3	170	230	210	1380	3,25	—
95	5	175	240	315	1380	3,32	—
93	7	180	245	320	1380	3,39	—
90	10	190	250	275	1390	3,47	—
85	15	195	255	320	1400	3,58	
80	20	200	260	330	1420	3,70	—
75	25	210	270	340	1430	3,83	Glass, crystal.
70	30	210	275	350	1450	3,96	Glass, crystal.
60	40	220	280	350	1450	4,25	Glass, crystal.

Thermal analysis of alloys of the As_2S_3-$CuCr_2Te_4$ system showed that thermograms of alloys are observed two endothermic effects related to solidus and three endothermic effects related to liquidus. DTA of the system alloys before annealing shows that on thermograms of the alloys in the concentration range of 0–25 mol. % $CuCr_2Te_4$, a softening temperature is observed at Tg of 170°C. After prolonged heat treatment at 170 ° C for 600 h, the alloys crystallize and a series of effects is observed on the thermograms.

a) b) c)

Fig. 1. Microstructure of alloys of the As_2S_3-$CuCr_2Te_4$ system.
a) - 1.5; b) -90.; c) - 96.5 mol % $CuCr_2Te_4$.

Microstructural analysis of the alloys of the As_2S_3-$CuCr_2Te_4$ system shows that, in addition to the initial components, the remaining alloys are biphasic. The microstructure of alloys from the region of 0-15 mol % $CuCr_2Te_4$ represents one phase of dark color, and in the concentration range from 15 to 25 mol. % $CuCr_2Te_4$ crystalline inclusions appears. A study of the microstructure of the annealed samples showed that 1.5 mol % $CuCr_2Te_4$ and 3.5 mol. % As_2S_3 single-phase alloys (Fig. 1a and c). As the content of $CuCr_2Te_4$ rises to 10 mol. % As_2S_3 solid solutions disintegrate and the alloys become biphasic (Fig. 1 b)

RAF of unannealed alloys of the As2S3-CuCr2Te4 system shows that only on thermograms of cast samples with a content of more than 25 mol. % CuCr2Te4, intense diffraction lines are observed. After annealing at 170°C for 600 hours on diffraction patterns in the concentration range of 0-25 mol % $CuCr_2Te_4$ intense diffraction maxima are obtained. X-ray analysis showed that the diffraction patterns of alloys 70 and 100 mol % $CuCr_2Te_4$ consist of mixed diffraction lines of the starting components. These data confirm that the alloys of the system are two-phased. Fig. 2 shows diffraction patterns of alloys in the system of compositions 10, 15, 25, 70, and 100 mol % $CuCr_2Te_4$. As seen in Fig. 1, alloys 10, 15 mol % CuCr2Te4 belongs to the field of glasses, 25 mol % CuCr2Te4 in the glass-crystalline region, 70 and 100 mol % $CuCr_2Te_4$ crystalline region.

DTA, XRD and MSA showed that in the system with slow cooling of the samples, the region of glass formation reaches 15 mol % $CuCr_2Te_4$, as well as in the regime of quenching in ice water of about 20 mol % $CuCr_2Te_4$.

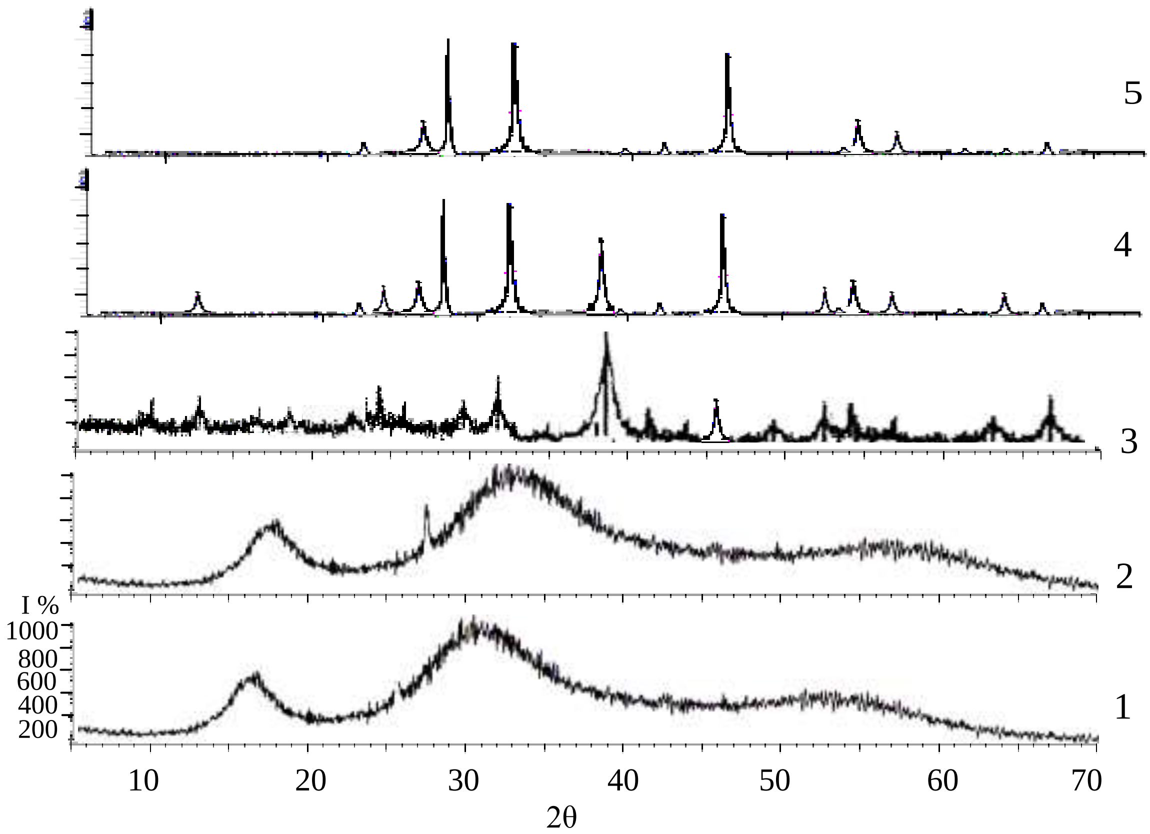

Fig. 2. Diffraction patterns of alloys of the As_2S_3-$CuCr_2Te_4$ system.
1-10, 2-15, 3-25, 4-70, 5-100 mol % $CuCr_2Te_4$.

The T-x phase diagram of the As_2S_3-$CuCr_2Te_4$ system built in line with the physicochemical analysis is shown in Fig. 3. The state diagram of the As_2S_3-$CuCr_2Te_4$ system is a quasi-binary eutectic type (Fig. 3).

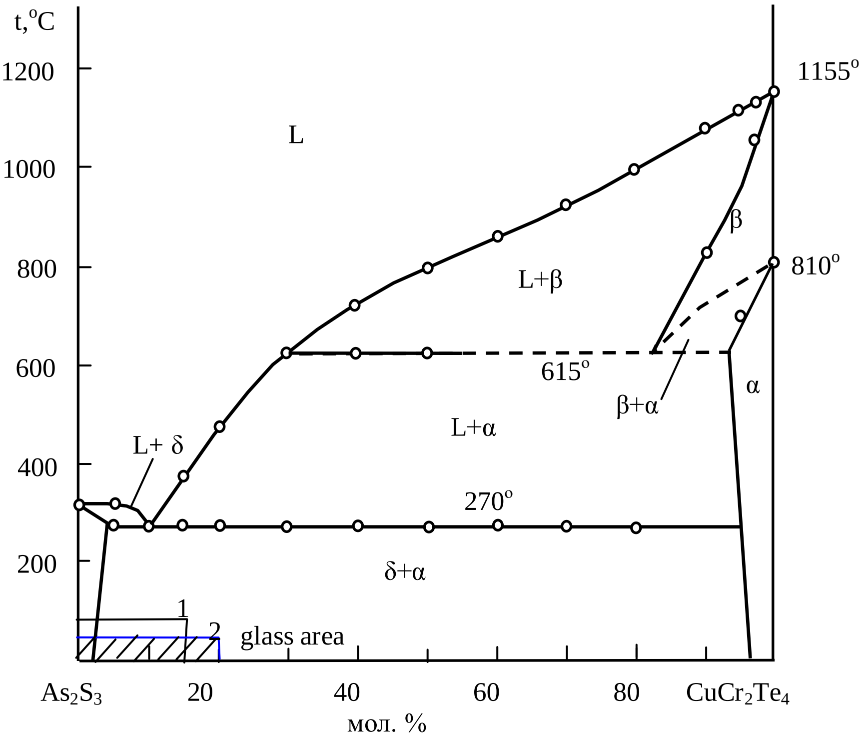

Fig. 3. T-x phase diagram of the As_2S_3-$CuCr_2Te_4$ system.
Area of glass formation: 1-slow cooling, 2-quenching in ice water.

The liquidus of the system consists of monovariant curves of δ, α and β-phase. The phases δ and α form an eutectic with composition of 10 mol % $CuCr_2Te_4$ and melt at 270 ° C. At the eutectic point, a three-phase reaction occurs: Ж↔ δ + α. In the range of 1.5-96 mol % $CuCr_2Te_4$ concentrations below the solidus line, two-phase alloys crystallize (δ + α). In the range of 96.5-100 mol % $CuCr_2Te_4$ crystallizes α phase. The microhardness of As_2S_3-$CuCr_2Te_4$ alloys was measured at each phase before and after annealing.

Table 2. Results of DTA measurements of microhardness and density of system alloys As_2S_3-$CuCr_2Te_4$ after annealing

Composition, mol %		Thermal effects, °C	Density, g/cm³	Microhardness, MPa	
				α	B
As_2S_3	$CuCr_2Te_4$			P=0,10 H	P=0,15 H
100	0.0	310	3,46	700	-
95	5,0	270,310	3,60	750	-
90	10	270	3,76	Eutec.	Eutec.
85	15	270,375	3,92	-	-
80	20	270,480	4,07	800	-
70	30	270,615	4,37	800	-
60	40	270,615,720	4,68	-	-
50	50	270, 615,800	4,98	-	-
40	60	270,860	5,28	-	1870
30	70	270,925	5,60	-	1870
20	80	270,1000	5,90	-	1880
10	90	830,1075	6,21	-	1880

5,0	95	700,1120	6,57	-	1880
3,0	97	1130	6,54	-	1860
0,0	100	810, 1155	6,51	-	1850

When measuring the microhardness of the system alloys, three series of values were obtained (Table 1). Before annealing, the microhardness of glassy alloys 0-10 mol % $CuCr_2Te_4$ in the range of microhardness varies in the range (1350-1400) MPa. After annealing the same alloys, the microhardness decreases (700-800) MPa. The microhardness of α phase ($CuCr_2Te_4$-based solid solutions) varies in the range (1850-1880) MPa. Prior to annealing, the density values of glassy alloys in the concentration range of 0–20 mol % $CuCr_2Te_4$ vary in the range of 3.20–3.70 g/cm^3 (Table 2). After annealing, the density values of the alloys in the same region vary within 3.46-3.93 g/cm^3 (Table 2). The data obtained show that the microhardness of glasses is higher than the corresponding crystals. On the contrary, the density of glasses is lower than that of the corresponding crystals, which is in good agreement with the literature.

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As_2S_3-$CuCr_2Te_4$ SİSTEMİNDƏ KİMYƏVİ QARŞILIQLI TƏSİR VƏ ŞÜŞƏƏMƏLƏGƏLMƏ

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As_2S_3-$CuCr_2Te_4$ sistemində kimyəvi qarşılıqlı təsir və şüşəəmləgəlmənin xüsusiyyətləri fiziki-kimyəvi analiz metodları (DTA, MSA, XRD, həmçinin sıxlıq və mikrobərkliyin ölçmələri) ilə tədqiq edilmiş və faza diaqramı qurulmuşdur. Nəticədə müəyyən edilmişdir ki, sistemin hal diaqramı kvazibinar olub, evtektik tiplidir. Sistemdə As_2S_3 yaxınlığındakı, 1.5 mol % -ə qədər məhdud sahədə bərk məhlul sahəsi mövcuddur, $CuCr_2Te_4$ birləşməsi əsasında isə 3.5 mol % bərk məhlul aşkar edilmişdir. As_2S_3 və $CuCr_2Te_4$ birləşmələri arasında əmələ gələn evtektikanın tərkibi 10 mol % $CuCr_2Te_4$ və ərimməsi isə 270°C-dir. As_2S_3-$CuCr_2Te_4$ sistemində adi soyudulma şəraitində, As_2S_3 əsasında şüşə sahəsi 15 mol % $CuCr_2Te_4$ təşkil edir.

Açar sözlər: *evtektik, şüşəəmələgəlmə, sıxlıq, mikrobərklik, sinqoniya.*

ХИМИЧЕСКОЕ ВЗАИМОДЕЙСТВИЕ И СТЕКЛООБРАЗОВАНИЕ В СИСТЕМЕ As_2S_3-$CuCr_2Te_4$

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Характер химического взаимодействия и стеклообразования в системе As_2S_3-$CuCr_2Te_4$ исследован методами физико-химического анализа (ДТА, МСА, РФА а также измерением плотности и микротвердости) и построена фазовая диаграмма. Установлено, что диаграмма состояния системы является квазибинарной эвтектического типа. В системе выявлены узкие гомогенные области до 1.5 мол. % As_2S_3 и 3.5 мол. %. $CuCr_2Te_4$. Соединения As_2S_3 и $CuCr_2Te_4$ между собой образуют эвтектику состава 10 мол. % $CuCr_2Te_4$ с температурой плавления 270°С. При обычных условиях охлаждения в системе As_2S_3-$CuCr_2Te_4$ на основе As_2S_3 область стеклообразования доходит до 15 мол. % $CuCr_2Te_4$.

Ключевые слова: *эвтектика, стеклообразование, плотность, микротвердость, сингония.*