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PHYSICO-CHEMICAL İNVESTİGATİON OF PHASE EQUILIBRIUM AND GLASS FORMATION IN THE AsS-$Cu_2Cr_4Te_7$ SYSTEM

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Abstract

Phase formation and vitrification in the AsS-$Cu_2Cr_4Te_7$ system are studied by the methods of physical and chemical analysis: differential thermal (DTA), X-ray diffraction (XRD), microstructural (MKA), and also determination of microhardness and density. The T-x phase diagram is constructed. It is established that the AsS-$Cu_2Cr_4Te_7$ system is a partially quasibinary section. Based on the results of the microstructural analysis, it was established that in the AsS-$Cu_2Cr_4Te_7$ system at room temperature, the solubility of 12 mol.% AsS based on the $Cu_2Cr_4Te_7$ compound was found, while the area of the solid solution based on the AsS compound is practically undefined. During slow cooling in the AsS-$Cu_2Cr_4Te_7$ system, a region of glass formed on the basis of AsS 10 mol. % $Cu_2Cr_4Te_7$. The area of AsS-based glass when cooled in ice water is 15 mol.% $Cu_2Cr_4Te_7$. In the interval of concentrations of 10–30 mol. % $Cu_2Cr_4Te_7$ there are alloys of glass crystal composition.

Keywords: peritectic, quasibinary, glass, solid solution, microhardness.

Introduction

Arsenic chalcogenides, one of the main elements of Group V, are known to form in a glassy state. Recently, arsenic chalcogenides, as well as complex glassy alloys and compounds based on them, have attracted the attention of researchers due to their unique functional properties. Arsenic chalcogenides, as well as complex glassy alloys and compounds based on them, are widely used in various fields of photoelectronics as photosensitive, luminescent, and acousto-optic materials [1–8]. Chromium chalcogenides form magnetic materials with a number of chalcogenides, including copper chalcogenides [9–15].

We have studied a number of systems involving the compound $Cu_2Cr_4Te_7$ [16, 17]. The physical properties of arsenic monosulfide AsS remain virtually unexplored. Therefore, it can be expected that new complex phases and glassy alloys obtained by the chemical interaction of AsS and $Cu_2Cr_4Te_7$ chalcogenides can also be semiconductor materials with magnetic and magneto-optical properties.

The aim of this work is to conduct a physicochemical study of the phase equilibrium in the AsS-$Cu_2Cr_4Te_7$ system, construct its phase diagram, and determine the glass transition and solid solution boundaries.

The glassy compound AsS melts at 318°C with an open maximum and crystallizes in the orthorhombic syngony, with lattice parameters: a = 9.32; b = 13.546; c = 6.585 Å [18]. The compound $Cu_2Cr_4Te_7$ melts incongruently at 1000°C and has a wide homogeneity region [15].

Experimental Section

The synthesis of AsS-$Cu_2Cr_4Te_7$ alloys was carried out in two stages. In the first stage, AsS and $Cu_2Cr_4Te_7$ compounds were synthesized using the ampoule method. The AsS compound was obtained from the elements in a single-zone furnace at a temperature of 400-700°C. The AsS compound was obtained as a glass with normal cooling. A two-zone furnace was used to obtain the $Cu_2Cr_4Te_7$ compound from the elements. To synthesize the $Cu_2Cr_4Te_7$ compound of the AsS-$Cu_2Cr_4Te_7$ system, elements taken in stoichiometric composition are placed in a 20-cm-long ampoule. To synthesize the $Cu_2Cr_4Te_7$ compound, part of the ampoule is inserted into a furnace at 1100°C. The remaining portion of the ampoule is left outside the furnace. During this process, Te vapor initially begins to form. This process continues until the Te vapor disappears. After maintaining the reaction at 1100°C for 3 hours, the furnace temperature is increased to 950°C, held for 4 hours, and then cooled by disconnecting it from the power source. In the second stage, the AsS-$Cu_2Cr_4Te_7$ alloys were synthesized from the AsS and $Cu_2Cr_4Te_7$ compounds using the ampoule method. The alloys of the system are then analyzed using physicochemical methods.

Differential-thermal analysis was performed on a Thermoscan-2 pyrometer. Chromel-alumel was used as a thermocouple, and the heating rate was 5°C/min.

Microstructural analysis was performed on an MIM-8 microscope. HNO3 + HF solutions (1:2) were used as etchants to reveal phase boundaries in the samples. X-ray phase analysis of the alloys was performed on a D2 PHASER X-ray diffractometer. CuKα radiation and a Ni filter were used as the anode.

Microhardness was measured on a PMT-3 metallographic microscope. Density was determined pycnometrically, using toluene as the filler solution.

Results and Discussion

Alloys of the AsS-$Cu_2Cr_4Te_7$ system are compact, and their color ranges from red to black. The alloys of the system are resistant to air, water, and organic solvents. They are highly soluble in strong acids (HNO_3, H_2SO_4). Alloys rich in AsS are soluble in alkalis (NaOH, KOH).

It should be noted that the physicochemical analyses of the alloys were carried out in both the crystalline and glassy states. Thermal analysis of the alloys before heat treatment revealed that thermal effects were observed in the thermograms of samples in the range of 0–15 mol. % $Cu_2Cr_4Te_7$ at a temperature of 170°C, which corresponds to the softening temperature of glass. The composition of the alloys of the system was studied by microstructural analysis, and it was found that there is a wide range of solubility in the region of the $Cu_2Cr_4Te_7$ compound. The microstructures of the alloys in the range of 0–15 mol. % $Cu_2Cr_4Te_7$ appear as opaque single-phase. Microstructural analysis revealed that only single-phase alloys were obtained based on the $Cu_2Cr_4Te_7$ compound. Figure 1 shows the microstructure of alloys with concentrations of 40, 70, and 90 mol. % $Cu_2Cr_4Te_7$. As can be seen from the figure, alloys with concentrations of 40 and 70 mol. % $Cu_2Cr_4Te_7$ are two-phase. The alloy with a concentration of 90 mol. % $Cu_2Cr_4Te_7$ is single-phase and represents a solid solution based on the $Cu_2Cr_4Te_7$ compound.

Fig. 1. Microstructure of AsS-$Cu_2Cr_4Te_7$ alloys.
1–40 mol. %, 2–70 mol. %, 4–90 mol. % $Cu_2Cr_4Te_7$.

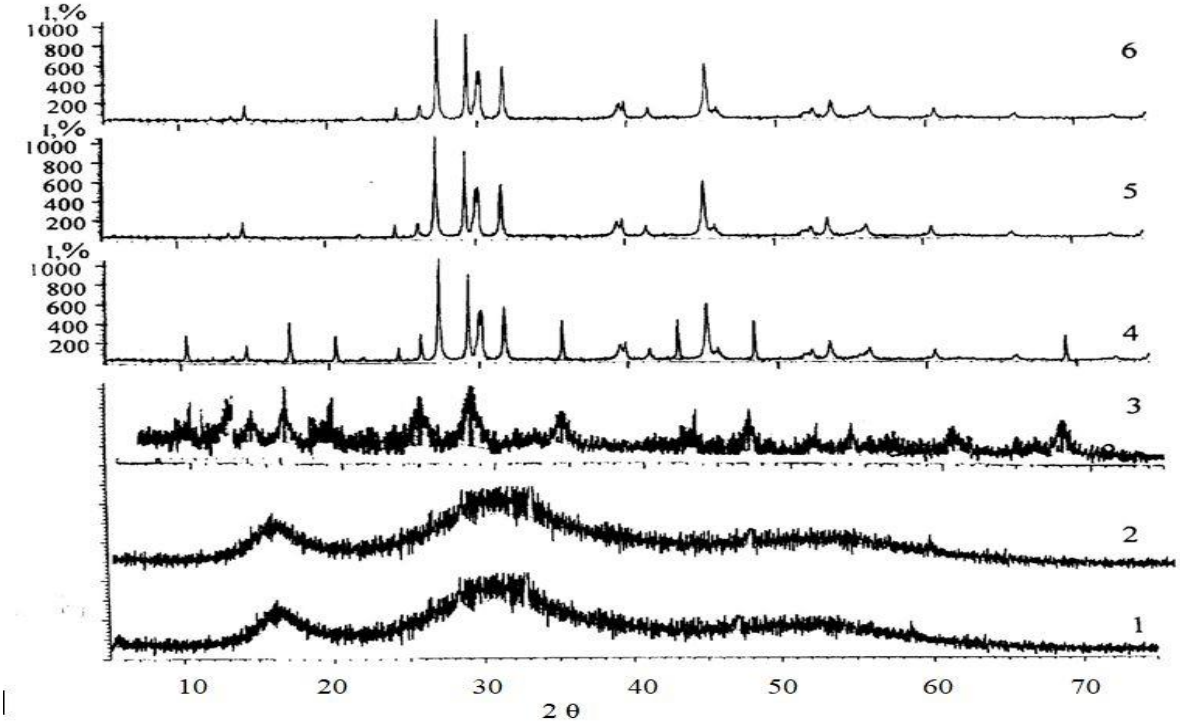

Fig. 2. X-ray diffraction patterns of AsS-$Cu_2Cr_4Te_7$ alloys.
1-5, 2-10, 3-30, 4-50, 5-90, 6-100 mol. % $Cu_2Cr_4Te_7$.

To clarify the results of differential thermal and microstructural analyses of AsS-$Cu_2Cr_4Te_7$ alloys, X-ray diffraction analysis was performed on alloys with contents of 5, 10, 30, 50, and 90 mol. % $Cu_2Cr_4Te_7$ (Fig. 2). Diffraction maxima in the diffraction patterns of alloys in the range of 0–30 mol.% $Cu_2Cr_4Te_7$ in the studied system revealed weak lines.

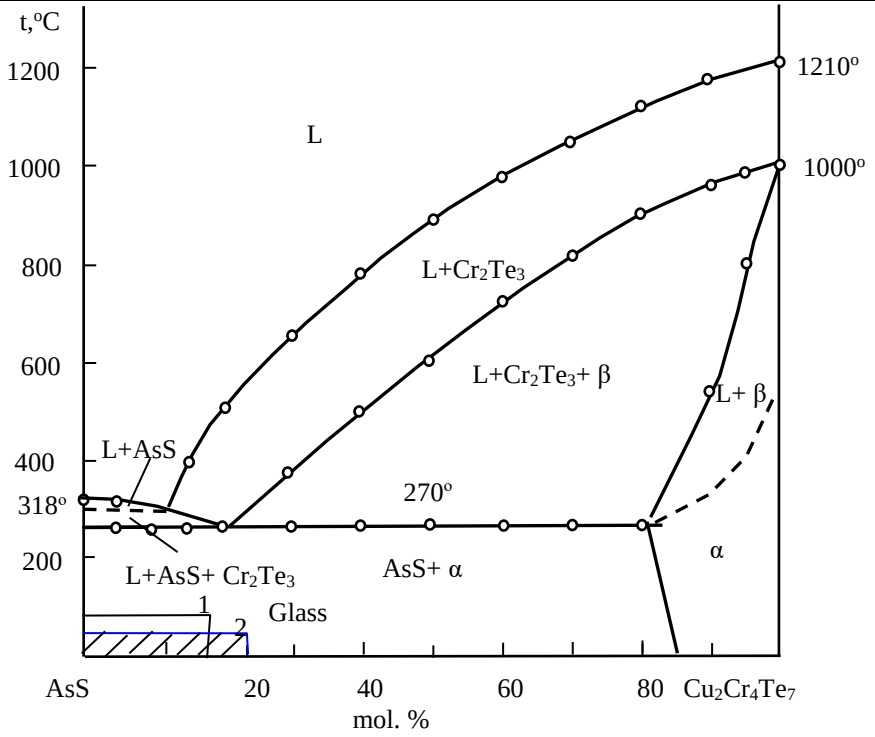

Fig.3. T-x phase diagram of the AsS-$Cu_2Cr_4Te_7$ system.
1- during slow cooling, 2- during cooling in ice water, glass area

Table 1.

Physico-chemical properties of glassy alloys of the AsS-$Cu_2Cr_4Te_7$ system (glass region)

Composition, mol. %		Thermal effects, °C			Microhardness, MPa	Density, q/cm³	MSA
AsS	$Cu_2Cr_4Te_7$	Tg	Tcrus.	Tmelt.			
100	0	170	220	318	1350	3,35	Şüşə
97	3	170	220	315	1380	3,55	—
95	5	175	230	315	1380	3,60	—
93	7	180	235	320	1380	3,67	—
90	10	190	240	270	1385	3,72	—
85	15	190	245	400	1390	3,90	Glass-crust
80	20	190	250	510	1400	4,10	Glass-crust
70	30	190	265	380	1430	4,47	Glass-crust
60	40	190	270	450	1440	4,85	crustal

This indicates the glassy nature of the samples in this region. Diffraction maxima were observed in the X-ray diffraction patterns of alloys containing 50 and 90 mol.% $Cu_2Cr_4Te_7$. Analysis revealed that the diffraction lines in the diffraction pattern of the sample containing 90 mol. % $Cu_2Cr_4Te_7$ are identical to those of the $Cu_2Cr_4Te_7$ compound, indicating that this sample is a solid solution alloy based on $Cu_2Cr_4Te_7$.

Based on the results of a comprehensive physicochemical analysis, a phase diagram of the AsS-$Cu_2Cr_4Te_7$ system was constructed (Fig. 3). In the AsS-$Cu_2Cr_4Te_7$ system, glassy AsS-based alloys with a composition of 10 mol. % $Cu_2Cr_4Te_7$ formed upon slow cooling. Alloys with a glassy-crystalline composition are present in the layer range of 10–30 mol. % $Cu_2Cr_4Te_7$. Table 1 shows the compositional dependences of the softening and crystallization temperatures, microhardness, and density of alloys from the glassy and glassy-crystalline regions. Table 2 presents some physicochemical properties of the alloys in the crystalline state of the system.

Table 2.

Composition, results of differential thermal analysis, determination of microhardness and density of AsS-$Cu_2Cr_4Te_7$ system alloys in crystalline form

Composition, mol. %		Thermal effects, ºC	Density, q/cm³	Microhardness, MPa	
AsS	$Cu_2Cr_4Te_7$			AsS	α
				0,15 H	0,20 H
100	0,0	318	3,52	660	-
95	5,0	270,315	3,60	700	-
90	10	270	3,75	720	-
85	15	270,400	4,05	740	-
80	20	270,510	4,24	-	-
70	30	270,380,650	4,59	-	-
60	40	270,450,780	4,95	-	2000
50	50	270,600,890	5,33	-	2000
40	60	270,720,975	5,67	-	2000
30	70	270, 810,1050	6,03	-	2000
20	80	270,900,1120	6,38	-	2000
10	90	545,960,1175	6,74	-	2000
5,0	95	800,980	7,22	-	2000
0,0	100	1000,1210	7,10	-	1970

The liquidus of the AsS-$Cu_2Cr_4Te_7$ system represents the initial crystallization curves of the β-solid solution obtained from $Cu_2Cr_4Te_7$. In the system, primary crystals of the AsS compound precipitate in the range of 0–20 mol. % $Cu_2Cr_4Te_7$. The system undergoes a process of eutectic equilibrium and peritectic transformation.

The decomposition of the $Cu_2Cr_4Te_7$ compound results in the formation of three-phase alloys consisting of (L + AsS + Cr_2Te_3) and (L + Cr_2Te_3 + β). Since the peritectic process L + Cr_2Te_3 ↔ $Cu_2Cr_4Te_7$ occurs, two-phase alloys consisting of AsS + α crystallize below the solidus line in the system.

The microhardness and density of AsS-$Cu_2Cr_4Te_7$ alloys were studied as a function of their composition in the glassy and crystalline states (Tables 1 and 2).

Two different microhardness values were determined in the system. Before heat treatment, i.e. in the glassy state, the microhardness and density of glasses obtained on the basis of AsS are Hμ=(1350-1440) MPa, ρ=(3.35-4.85) g/cm^3, for α-solid solutions based on the compound $Cu_2Cr_4Te_7$ the microhardness is Hμ=(2750-2800) MPa, and the density ρ=3.52-7.22 g/cm^3. After heat treatment, the microhardness of samples from the glassy region is Hμ=(660-740) MPa, ρ=(3.53-4.59) g/cm^3. The microhardness and density of the crystalline phases do not change. It was found that during the glass-crystal transition the hardness of the alloys decreases and their specific gravity increases.

Conclusion

Thus, based on the results of comprehensive physicochemical analysis methods, a phase diagram of the AsS-$Cu_2Cr_4Te_7$ system has been constructed. The phase diagram of the system is partially quasi-binary and belongs to the eutectic type. The system undergoes eutectic equilibrium and peritectic transformation, leading to the crystallization of two-phase alloys of the AsS + α composition below the solidus line.

In the AsS-$Cu_2Cr_4Te_7$ system, the AsS-based solid solution region is virtually undefined. The Cu2Cr4Te7-based solid solution region is 15 mol. % AsS. The glass transition region of the AsS-based system under normal conditions is determined to be 10 mol. % $Cu_2Cr_4Te_7$. After cooling in ice water, the glass transition region of the AsS-based system is 15 mol. % $Cu_2Cr_4Te_7$. The dependence of the softening temperature Tg, crystallization Tcrys., microhardness and density of glassy region alloys on the composition was studied.

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