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CHARACTER OF CHEMICAL INTERACTION IN THE Bi_2Se_3-$CuCr_2Te_4$ SYSTEM AND X-RAY STUDY OF THE OBTAINED COMPOSITE MATERIALS

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Abstract

Using physical and chemical analysis methods (DTA, MSA, X-raydifraction, as well as density and microhardness measurements), the nature of the chemical interaction in the Bi_2Se_3-$CuCr_2Te_4$ system was studied and phase diagram was constructed. It has been established that the phase diagram of the system is quasi-binary and eutectic. The binary eutectic formed between the compounds Bi_2Se_3 and $CuCr_2Te_4$ has a content of 25 mol % $CuCr_2Te_4$ and temperature 530°C. According to the results of microstructural analysis, in a system based on the Bi_2Se_3 compound, a 5 mol % $CuCr_2Te_4$ solid solution region is formed, and based on the $CuCr_2Te_4$ compound, 8 mol % Bi_2Se_3 is dissolved. X-ray phase analysis of solid solutions $(CuCr_2Te_4)_{1-x}(Bi_2Se_3)_x$ (x=0.02; 0.05; 0.08) was carried out and their lattice parameters were calculated. It has been established that alloys containing 2, 5 and 8 mol % $CuCr_2Te_4$ crystallize in the cubic syngony, lattice parameters: *a*=11.245 Å, *a*=11.288 Å, *a*=11.346 Å, respectively.

Keywords: composite material, system, phase diagram, topological insulator, density

Introduction

Recently there has been some interest in complex chalcogenide compounds. This is due, first of all, to the extensive study of the chemistry and physics of these compounds and the increase in their practical application. It is known that bismuth chalcogenides, compounds and solid solutions based on them are valuable thermoelectric materials that convert electrical energy into thermal energy [1-9].

Recently, the attention of researchers working in the field of semiconductors has been attracted by new topological insulator materials based on layered compounds, including bismuth chalcogenides [10-14]. Therefore, the search for thermoelectric materials to create alternative energy sources is of scientific and practical importance. A large number of ternary and more complex systems have been studied based on bismuth chalcogenides [15-19]. Spinel-type compounds $CuCr_2X_4$ (X-S,Se,Te) based on copper and chromium chalcogenides are widely studied as ferromagnetic materials [20-22].

The purpose of this work is to study the nature of the chemical interaction in the Bi_2Se_3-$CuCr_2Te_4$ system, construct its phase diagram and x-ray studies of the resulting composite materials.

The Bi_2Se_3 compound melts congruently at 706°C and crystallizes into rhombohedral syngony with a lattice parameter *a*=9.832 Å. $\alpha=24^o10'$, sp. gr. $P3m\text{-}D^5_{3d}$, density $\rho=8.0\ g/cm^3$, microhardness $H\mu=850$ MPa [23]. The $CuCr_2Te_4$ compound melts congruently at 1155°C and crystallizes in the cubic syngony, lattice parameter *a* = 11.134 Å [24]. The phase transition of the $CuCr_2Te_4$ compound occurs at a temperature of 810°C.

Experimental part

Alloys of the Bi_2Se_3-$CuCr_2Te_4$ systems were synthesized from the components Bi_2Se_3 and $CuCr_2Te_4$ in the temperature range 800-1200°C in a single-temperature vertical furnace using the ampoule method.

The alloys were subjected to heat treatment for 240 hours at a temperature of 500°C to homogenize them. Then the alloys of the Bi_2Se_3-$CuCr_2Te_4$ systems were studied by methods of physical and chemical analysis: differential thermal analysis (DTA), X-ray diffraction (XRD), microstructural analysis (MSA), as well as methods of measuring density and microhardness.

Differential-thermal analysis (DTA) was carried out using a TERMOSCAN-2 thermograph. The Al_2O_3 compound was taken as standard, the heating rate was 5 K/min.

X-ray phase analysis was carried out on a D2-PHASER X-ray diffractometer. The study used CuKα radiation and a Ni filter.

Microstructural analysis (MSA) was carried out on a MIM-8 microscope. To do this, the alloys were polished and given shine, and their structure was examined under a microscope. To clarify the phase boundaries, a solution of 10 ml of H_2SO_4 + 5 ml of $K_2Cr_2O_7$ was taken. Microhardness was measured with a PMT-3 metallographic hardness tester. The compositional dependence of microhardness for each phase was measured. The density of the samples was determined by the pycnometric method; toluene was used as a filling solution.

Results and its discussion

Alloys of the Bi_2Se_3-$CuCr_2Te_4$ system have a compact mass of bright gray color. Samples rich in the $CuCr_2Te_4$ compound are black in color.

The results of differential-thermal analysis show that endothermic effects are similar to those obtained from thermograms of alloys. There are two and three endothermic effects in the thermograms of alloys. As a result of microstructural analysis of the alloys, it was established that there is a single-phase region around the Bi_2Se_3 and $CuCr_2Te_4$ compounds in the system, while the remaining alloys are two-phase.

Based on the results of physicochemical analysis methods, the microstructure of alloys of the Bi_2Se_3-$CuCr_2Te_4$ system is presented in Fig. 1.

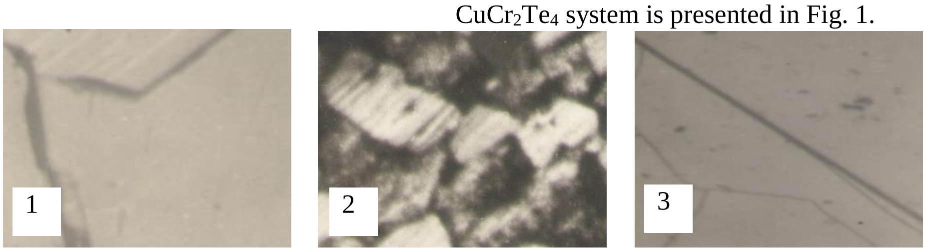

Fig. 1. Microstructures of alloys of the Bi_2Se_3-$CuCr_2Te_4$ system.
1-5 mol %, 2-70 mol%, 92 mol % $CuCr_2Te_4$,

Samples containing 5 and 92 mol % $CuCr_2Te_4$ are single-phase solid solutions based on Bi_2Se_3 and $CuCr_2Te_4$ compounds, respectively. A sample with a concentration of 70 mol. % $CuCr_2Te_4$ is two phase.

To confirm the results of differential thermal and microstructural analysis, X-ray phase analysis of samples containing 5, 70 and 92 mol % $CuCr_2Te_4$ of the Bi_2Se_3-$CuCr_2Te_4$ system of the same composition (Fig. 2). The X-ray patterns of the samples were then compared with the X-ray patterns of the original components. As can be seen from Fig. 2, diffraction lines present in the diffraction patterns of samples 5 and 92 mol % $CuCr_2Te_4$ are identical to the diffraction patterns of the compounds Bi_2Se_3 and $CuCr_2Te_4$, respectively. That is, these samples are solid solution alloys based on Bi_2Se_3 and $CuCr_2Te_4$ compounds. Diffraction lines in the diffraction pattern of a 70 mol % $CuCr_2Te_4$ sample are a two-phase alloy consisting of a mixture of diffraction lines of the original compounds.

Thus, X-ray phase analysis confirms the results of DTA and microstructural analysis.

Based on the results of physical and chemical analysis methods, a T-x phase diagram of the system was constructed, which is presented in Figure 3. The phase diagram of the Bi_2Se_3-$CuCr_2Te_4$ system is quasi-binary, eutectic type. The composition of the eutectic formed between the compounds Bi_2Se_3 and $CuCr_2Te_4$ is 25 mol % $CuCr_2Te_4$, temperature 530°C.

The liquidus of the Bi_2Se_3-$CuCr_2Te_4$ system consists of the primary crystallization curves of the δ-solid solution formed based on Bi_2Se_3 and the α-solid solution based on $CuCr_2Te_4$. In the system at room temperature on the basis of the compound Bi_2Se_3, the solubility of 5 mol % $CuCr_2Te_4$, was detected and on the basis of the compound $CuCr_2Te_4$, the area of the solid solution is 8 mol % Bi_2Se_3. In the Bi_2Se_3-$CuCr_2Te_4$ system, two-phase alloys consisting of (δ + α) crystallize below the solidus line.

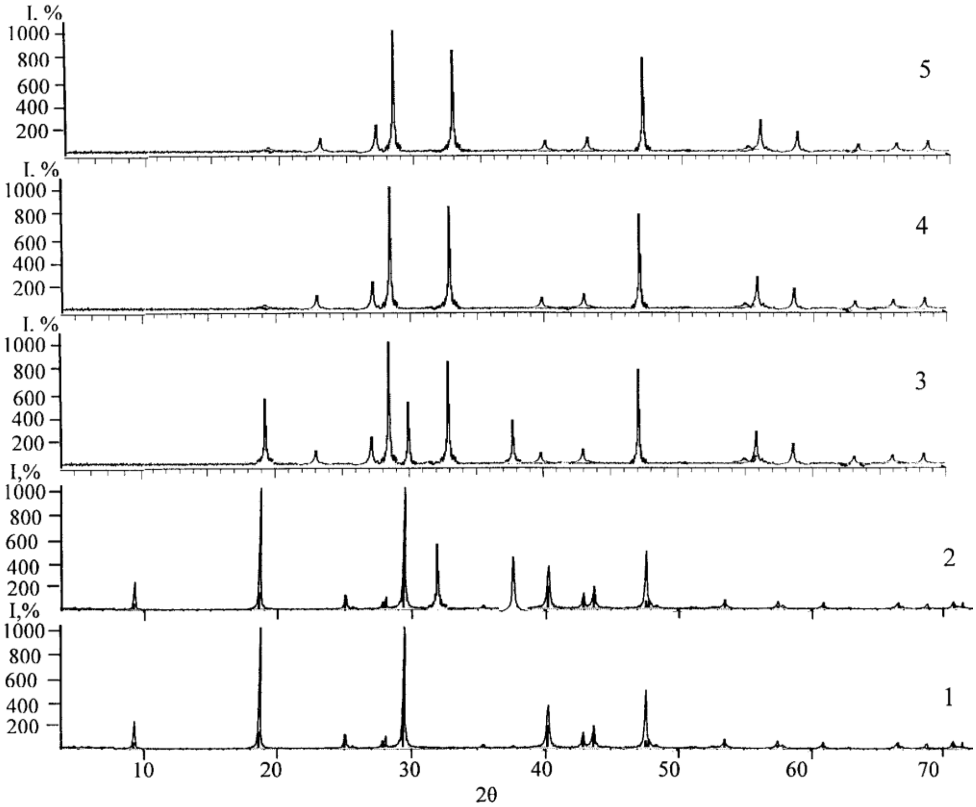

Fig. 2. X-ray diffraction patterns of alloys of the Bi_2Se_3-$CuCr_2Te_4$ system.
1-Bi_2Se_3, 2-5 mol %, 3-70 mol %, 6-92 mol %, 5-100 mol % $CuCr_2Te_4$

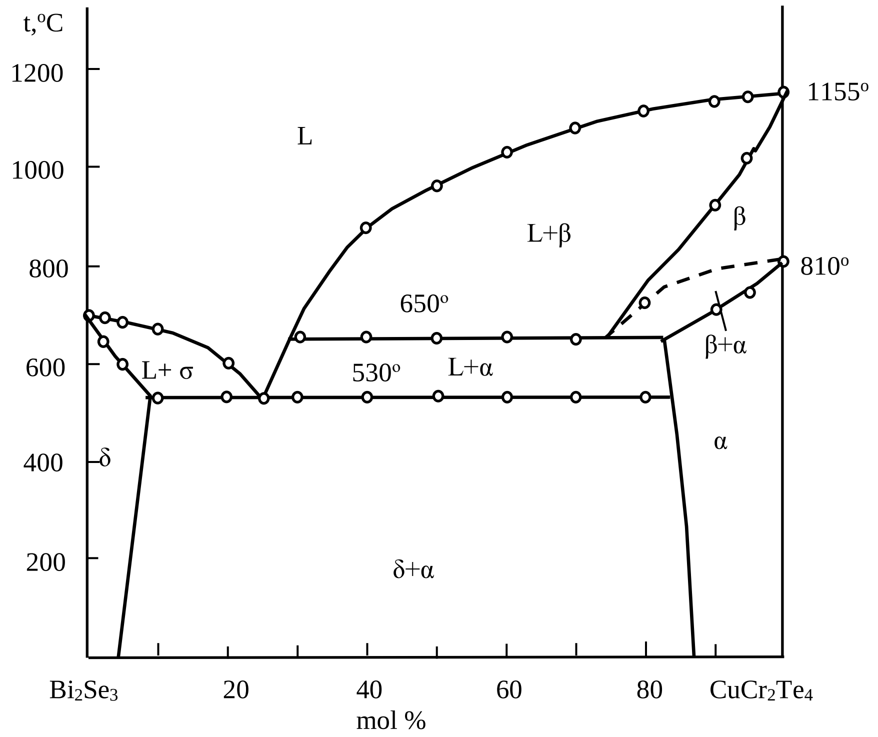

Fig.3. T-x phase diagram of the Bi_2Se_3-$CuCr_2Te_4$ system.

Table 1.

Composition of alloys of the Bi_2Se_3-$CuCr_2Te_4$ system, results of DTA, density and microhardness measurements

Composition, mol %		Thermal effects, °C	Density, q/sm³	Microhardness, MPa	
Bi_2Se_3	$CuCr_2Te_4$			δ	α
				P=0,10 N	P=0,15 N
100	0.0	706	8,00	850	–
97	3,0	650,700	8,06	890	–
95	5,0	600,690	8,12	900	–
90	10	530,675	8,00	900	–
80	20	530,600	7,90	900	–
75	25	530	7,72	–	–
70	30	530,650	7,55	Eutek.	Eutek.
60	40	530,650,880	7,40	–	2000
50	50	530,650,970	7,30	–	2000
40	60	530,650,1040	7,10	–	2000
30	70	530,650,1080	6,95	–	2000
20	80	530,725,1120	6,80	–	2000
10	90	710,925,1140	6,65	–	2000
5,0	95	750,1025,1150	6,58	–	1870
0,0	100	810, 1155	6,51	–	1850

The dependence of the microhardness of alloys of the Bi_2Se_3-$CuCr_2Te_4$ system on composition has been studied and it has been established that there are two different values of microhardness. Some physicochemical properties of the system are given in Table 1. The microhardness value (850-900) MPa corresponds to the microhardness of δ-solid solutions based on the Bi_2Se_3 compound. The microhardness of α-solid solutions based on the $CuCr_2Te_4$ compound varies within the range (1850-2000) MPa.

To clarify the region of the $(CuCr_2Te_4)_{1-x}(Bi_2Se_3)_x$ solid solution, X-ray phase analysis of alloys containing 2, 5 and 8 mol % $CuCr_2Te_4$, and their lattice parameters were calculated. The results of X-ray phase analysis show that solid solution alloys based on $CuCr_2Te_4$ also crystallize in the cubic syngony. As a result, it was found that with an increase in the amount of Bi_2Se_3 compound 2, 5 and 8 mol % $CuCr_2Te_4$ lattice parameters increase significantly in lattice parameter for: *a*=11.245 Å, *a*=11.288 Å, *a*=11.346 Å, Crystallographic results of samples containing 3, 5 and 8 mol % $CuCr_2Te_4$ are given in table. 2.

Table 2.

X-ray data of solid solutions $(CuCr_2Te_4)_{1-x}(Bi_2Se_3)_x$ (x=0,02; 0,05; 0,08)

$CuCr_2Te_4$ *a*=11,134 Å					98 **$CuCr_2Te_4$** -2 % **Bi_2Se_3** *a*= 11,245 Å				
I,%	$d_{təc.}$, Å	h	k	l	I,%	$d_{təc.}$, Å	h	k	l
8	3,9386	2	2	0	9	3,9726	2	2	0
23	3,3588	3	1	1	25	3,3928	3	1	1
100	3,2158	2	2	2	100	3,2498	2	2	2
95	2,7850	4	0	0	95	2,8190	4	0	0
3	2,2739	4	2	2	3	2,3079	4	2	2
8	2,1439	5	1	1	8	2,1779	5	1	1
90	1,9693	4	4	0	3	2,0033	4	4	0
2	1,6988	5	3	3	2	1,7328	5	3	3
35	1,6794	6	2	2	35	1,7134	6	2	2
18	1,6079	4	4	4	20	1,6519	4	4	4
2	1,4886	6	6	2	3	1,5226	6	6	2
3	1,4503	7	5	1	5	1,4843	7	5	1
11	1,3925	8	0	0	12	1,4255	8	0	0
95 **$CuCr_2Te_4$** -5 % **Bi_2Se_3** *a*=11,288 Å					92 **$CuCr_2Te_4$**-8 % **Bi_2Se_3** *a*=11,346 Å				
I,%	$d_{təc.}$, Å	h	k	l	I,%	$d_{təc.}$, Å	h	k	l
9	3,9846	2	2	0	9	3,9903	2	2	0
25	3,4048	3	1	1	25	3,4105	3	1	1
100	3,2618	2	2	2	100	3,2675	2	2	2
95	2,8310	4	0	0	95	2,8367	4	0	0
3	2,3199	4	2	2	5	2,7909	4	2	2
8	2,1898	5	1	1	8	2,1956	5	1	1
90	2,0153	4	4	0	90	2,0210	4	4	0
2	1,7558	5	3	3	4	1,7505	5	3	3
35	1,7254	6	2	2	35	1,7311	6	2	2
20	1,6539	4	4	4	20	1,6596	4	4	4
3	1,5346	6	6	2	3	1,5403	6	6	2
5	1,4963	7	5	1	7	1,5020	7	5	1
12	1,4385	8	0	0	12	1,4442	8	0	0

Conclusion

Using complex methods of physicochemical analysis, the chemical interaction in the Bi_2Se_3-$CuCr_2Te_4$ system was studied and its T-x phase diagram was constructed. It has been established that the phase diagram of the Bi_2Se_3-$CuCr_2Te_4$ system is a quasi-binary section of the quasi-ternary system Bi_2Se_3-$CuCr_2Te_4$ and belongs to the eutectic type. Cocrystallization of the Bi_2Se_3 and $CuCr_2Te_4$ compounds ends at the double eutectic point, coordinate: 25 mol % $CuCr_2Te_4$, temperature 530°C. In the Bi_2Se_3-$CuCr_2Te_4$ system at room temperature, solid solutions based on the Bi_2Se_3 compound make up 5 mol % $CuCr_2Te_4$, and on the basis of $CuCr_2Te_4$ up to 8 mol % Bi_2Se_3. X-ray phase analysis of solid solutions $(CuCr_2Te_4)_{1-x}(Bi_2Se_3)_x$ (x=0.02; 0.05; 0.08) was carried out and their lattice parameters were calculated. It has been established that alloys containing 2, 5 and 8 mol % $CuCr_2Te_4$, crystallize in a cubic syngony with lattice parameters: a=11.245 Å, a=11.288 Å, a=11.346 Å, respectively.

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