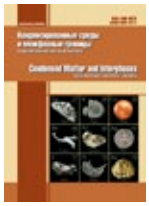

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Physicochemical study of phase formation in the Sb_2S_3-Cr_2Te_3 system

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Abstract

Chromium chalcogenides and systems based on them have not been sufficiently studied. Chromium chalcogenide compounds Cr_2X_3 (X = S, Se, Te), new phases and solid solutions based on them are widely used in semiconductor technology, since these are materials with thermoelectric and magnetic properties. The purpose of this study was the investigation of chemical interactions in the Sb_2S_3–Cr_2Te_3 system, the construction of a phase diagram, and the search for new phases and solid solutions.

Using the methods of physicochemical analysis (differential thermal, X-ray phase, microstructural analysis, as well as density and microhardness measurements), the chemical interaction in the Sb_2S_3-Cr_2Te_3 system was studied and its phase diagram was constructed. The phase diagram of the system is quasi-binary and is characterized by the formation of a quaternary compound $Cr_2Sb_2S_3Te_3$.

Compound $Cr_2Sb_2S_3Te_3$ incongruently melted at 610 °C. Microstructural analysis showed that at room temperature solid solutions based on Sb_2S_3 were formed in the system, which reached up to 5 mol. % Cr_2Te_3, and based on Cr_2Te_3 up to – 8 mol. % Sb_2S_3. The Sb_2S_3–Cr_2Te_3 eutectic formed in the Sb system contains 20 mol. %Cr_2Te_3 and has a melting point of 430 °C. The $Cr_2Sb_2S_3Te_3$ compound crystallizes in a tetragonal system with the unit cell parameters: a = 10.03; c =16. 67 Å, z = 7, $\rho_{pycn.}$ = 5.72 g/cm^3, $\rho_{X\text{-}ray}$ = 5.765g/cm^3.

Keywords: System, Phase, Solid solution, Eutectic, Syngony

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1. Introduction

The search for functional materials that can meet the ever-increasing needs of the electronics industry is always in the spotlight. Materials that meet these requirements include antimony chalcogenide compounds and alloys based on them. Antimony sulfides and selenides are used in optical systems as photosensitive materials [1–7]. Antimony tellurides are materials with thermoelectric properties, used as energy converters [8–15].

It is known that the element chromium and chalcogenide compounds are used, not only for the manufacture of magnetic materials, but also for the production of ferrimagnets of complex composition with other chalcogenides. Ternary and more complex compounds based on chromium chalcogenides have high ferromagnetic properties [16–19]. Therefore, the production of photosensitive and magneto-optical materials that retain the properties of the original compounds via the chemical interaction of photosensitive antimony chalcogenides with magnetic chromium chalcogenides is of both scientific and practical importance.

The Sb_2S_3 compound melts congruently at 559.5 °C and crystallizes in the orthorhombic system with lattice parameters: a = 11. 229; b = 11.310; c = 3.83 Å, space gr. $Pbnm$-D^{16}_{2h}, density 4.63 g/cm^3, microhardness 1400 MPa [20]. The Cr_2Te_3 compound melts congruently at 1280 °C and crystallizes in a hexagonal system with lattice parameters: a = 6.811; c = 12.062 Å, space gr. *hP20 - P31c* [21]. Phase transition α-Cr_2Te_3 has a temperature of 480 °C.

2. Experimental

Alloys of Sb_2S_3–Cr_2Te_3 were synthesized from Sb_2S_3 and Cr_2Te_3 components in an evacuated quartz ampoule at a pressure of 0.133 Pa in the temperature range 600–1100 °C. The samples were heat treated at 500 °C for 240 h to ensure equilibrium.

Equilibrium alloys were studied by differential thermal analysis (DTA), X-ray diffraction (XRD), microstructural analysis (MSA), as well as by microhardness and density measurements.

DTA analysis of the samples was carried out using a frequency pyrometer NTR-73, the error was ±5 °C. The reordering of heating and cooling curves were carried using an N. S. Kurnakov NTR-73 pyrometer. The studied substance was placed in a quartz ampoule with the length of 0.10–0.11 m and diameter·$8–10·10^{-3}$ m, which was pumped out to 0.1333 Pa and sealed. A thermocouple passed through a hole of the ceramic block with corresponding diameter was placed bellow the sample. The tubular furnace, inside which a steel block was placed was used for heating. NaCl, KCl, Na_2SO_4, K_2SO_4 were used as reference compounds. Heating and cooling curves of these compounds were recorded under similar conditions with a heating rate of 10 °C/min. Based on the data obtained for the reference substances, a calibration curve was constructed and checked after 15 days. The study mainly analyzed the thermal effects detected in the heating curves. Chromel-alumel was used as a thermocouple.

XRD was carried out using D2 PHASER X-ray device in CuK_α- radiation with a Ni filter.

Microstructure analysis (MSA) was performed by microscopic study using MIM-8 microscope. The solution 1 N HNO_3: H_2O_2 = 1: 1 was used as a clarifier to determine phase boundaries. Microhardness was measured using a PMT-3 metallographic microscope. The density of the samples was determined by the pycnometric method; toluene was used as a filler.

3. Results and discussion

Sb_2S_3-rich samples easily melted, forming a compact mass. After synthesis, Cr_2Te_3 compound was formed in the form of heterogeneous ingots. Therefore, the heterogeneous ingot was crushed into powder, pressed under a pressure of 200 atm and obtained in the form of tablets. In tablet form, the sample was placed in a quartz ampoule and sealed by sucking out the air and melting it in a gas lamp. Then solid-phase synthesis was carried out by heating the sample at a temperature of 800 °C for 100 h. After verification of the formation of Cr_2Te_3 compound, alloys of the Sb_2S_3–Cr_2Te_3 system were synthesized.

The alloys of the Sb_2S_3–Cr_2Te_3 system were studied using physicochemical analysis methods. According to DTA data, it was established that two and three endothermic effects were obtained in the thermograms of the alloys.

After a phase analysis of the alloys of the system, it was found that the alloys in proximity to the initial components and containing 50 mol. % Cr_2Te_3 are single-phase. At a content above 5 mol. % Cr_2Te_3 the second phase was formed, i.e., two-phase regions appeared (Fig. 1b). The microstructures of alloys containing 5, 10, and 50 mol. % Cr_2Te_3 Sb of Sb_2S_3–Cr_2Te_3 systems are shown in Fig. 1. As can be seen, 2 mol. % Cr_2Te_3 and the sample with 50 mol. % Cr_2Te_3 were single-phase solid solutions (Fig. 1a, c). The sample containing 10 mol. % Cr_2Te_3 has two-phases (Fig. 1b).

For the conformation of DTA and MSA results, X-ray phase analysis of alloys of 30, 50 and 92 mol. % Cr_2Te_3 of the Sb_2S_3–Cr_2Te_3 systems was performed (Fig. 2). As can be seen from Fig. 2, diffraction lines of the sample 92 mol. % Cr_2Te_3 did not differ from the X-ray diffraction pattern of the Cr_2Te_3 compound, and a slight shift is observed. This sample is a solid solution based

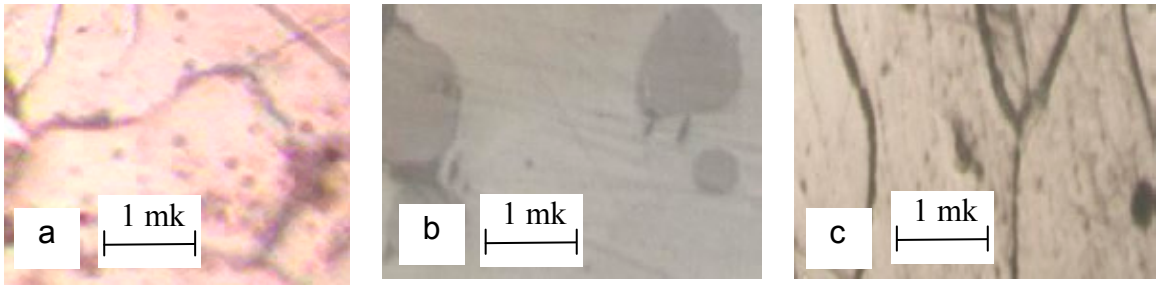

Fig. 1. Microstructures of alloys of Sb_2S_3-Cr_2Te_3 system (×340): a) – 5 mol %; b) – 10 mol %; c) – 50 ($Cr_2Sb_2S_3Te_3$) mol % Cr_2Te_3

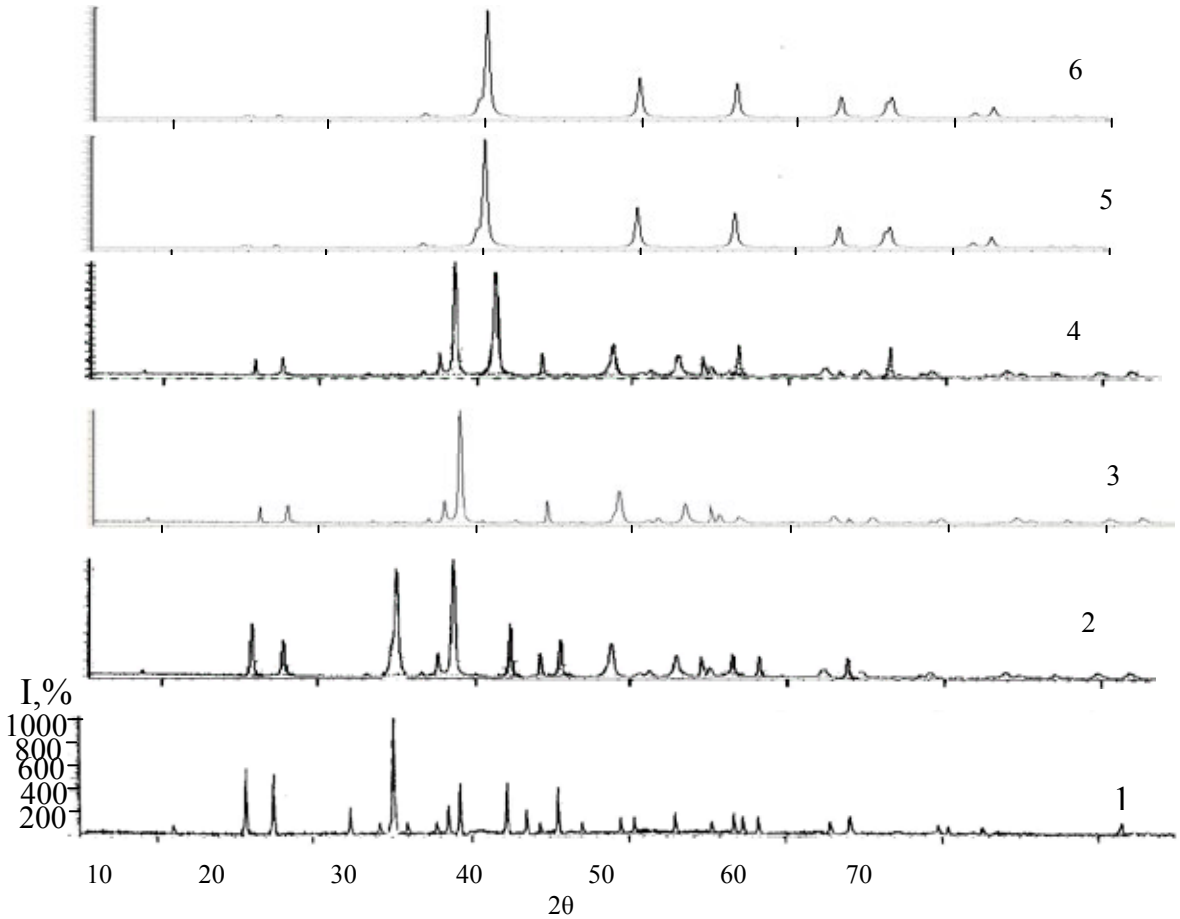

Fig. 2. Diffraction patterns of system alloys of Sb_2S_3–Cr_2Te_3 system: *1* – Sb_2S_3; 2 – 30; *3* – 50 ($Cr_2Sb_2S_3Te_3$); *4* – 70; *5* – 92; *6* – 100 mol. % Cr_2Te_3

on Cr_2Te_3. In the diffraction patterns of samples with 30 and 70 mol. % Cr_2Te_3 diffraction lines of the original components were present, i.e. the samples were two-phase.

Diffraction peaks in the diffraction pattern of a sample containing 50 mol. % Cr_2Te_3, differed from the diffraction lines in the diffraction patterns of the original components by interplanar distances and intensity. As a result, a new quaternary compound containing $Cr_2Sb_2S_3Te_3$ was obtained (Fig. 2). The $Cr_2Sb_2S_3Te_3$ compound can be considered as a derivative of $CrSbTe_3$, obtained by anionic substitution of $Cr_2Sb_2S_3Te_3$ (abbreviated as $CrSbS_{1.5}Te_{1.5}$).

As a result of physicochemical analysis, a quasi-binary phase diagram of the Sb_2S_3-Cr_2Te_3 system was constructed (Fig. 3). The $Cr_2Sb_2S_3Te_3$ compound was formed as a result of a peritectic reaction: F + Cr_2Te_3 ↔$Cr_2Sb_2S_3Te_3$ at 610 °C.

Liquidus of Sb_2S_3-Cr_2Te_3 system consisted of monovariant equilibrium curves for an α-solid solution based on the Sb_2S_3 compound, a new compound $Cr_2Sb_2S_3Te$ and β-solid solution based on Cr_2Te_3 compound. The binary eutectic formed in the system has a Cr_2Te_3 content of 20 mol. % and melting point 430 °C.

Crystallization of the α-solid solution was completed in the system in the concentration range of 0-20 mol. % Cr_2Te_3. In the range of 0–20 mol. % Cr_2Te_3 two-phase alloys (L + δ) were below the liquidus curve (Fig. 3). Two-phase alloys consisting of (δ + $Cr_2Sb_2S_3Te_3$), below the solidus line crystallized in the region of 5–50 mol. % Cr_2Te_3. In the concentration range of 50–92 mol. % Cr_2Te_3, two-phase alloys ($Cr_2Sb_2S_3Te$ + α) were below the solidus line. Some physicochemical properties of the alloys are shown in Table 1.

As a result of microhardness measurements, three different values were obtained. The microhardness value (1400–1470) MPa corresponded to the microhardness of an α-solid solution based on Sb_2S_3. The microhardness value (1750–1880) MPa corresponded to the microhardness of the $Cr_2Sb_2S_3Te_3$ compound, and the value (2070–2150) MPa corresponded to the microhardness of the β-solid solution based on Cr_2Te_3. The dependence of the density of the alloys of the system on the composition showed that no sharp change was observed.

Based on the results of X-ray phase analysis, it was established that the $Cr_2Sb_2S_3Te_3$

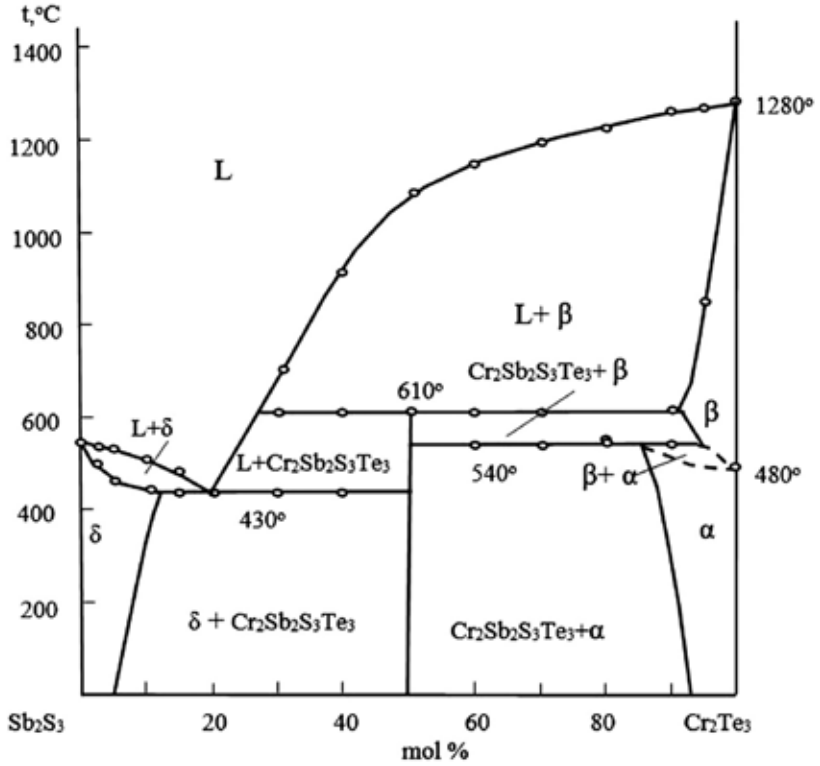

Fig. 3. Phase diagram of the Sb_2S_3–Cr_2Te_3 system

Table 1. Composition of alloys of the Sb_2S_3–Cr_2Te_3 system, DTA results, determination of microhardness and density

Composition, mol. %		Thermal effects, °C	Density, 10^3 kg/m^3	Microhardness, MPa		
Sb_2S_3	Cr_2Te_3			α	$Sb_2Cr_2S_3Te_3$	β
				P = 0.1 H		P = 0.2 H
100	0.0	560	4.63	1400	–	–
97	3.0	500, 555	4.70	1450	–	–
95	5.0	470, 530	4.78	1470	–	–
90	10	440, 515	4.86	1470	–	–
85	15	430, 480	4.97	–	–	–
80	20	430	5.06	eutectic	eutectic	–
70	30	430, 610, 700	5.29	–	–	–
60	40	430, 610, 920	5.51	–	1750	–
50	50	610, 1090	5.72	–	1750	3280
40	60	540, 610, 1150	5.94	–	1800	3280
30	70	540, 610, 1195	6.16	–	1850	3280
20	80	540, 610, 1230	6.39	–	1880	3280
10	90	540, 610, 1260	6.65	–	–	3280
5.0	95	850, 1270	6.83	–	–	3280
0.0	100	480, 1280	6.82	–	–	3250

Table 2. Interplanar distances (d), intensity (I) of lines and lattice indices (hkl) in the diffraction pattern of the $Cr_2Sb_2S_3Te_3$ compound

No	I, %	$d_{exp.}$, Å	$d_{cal.}$, Å	$1/d^2_{exp.}$, Å	$1/d^2_{cal.}$, Å	hkl
1	5.9	10.0289	10.0289	0.0099	0.0099	100
2	15.8	5.5561	5.5561	0.0324	0.0324	003
3	17.4	5.0252	5.0125	0.0396	0.0398	200
4	4.1	3.8528	3.8490	0.0674	0.0675	104
5	6.1	3.3509	3.3445	0.0891	0.0894	300
6	22.5	3.2277	3.2042	0.0960	0.0974	204
7	100	3.1236	3.1159	0.1025	0.1030	311
8	4.4	2.7857	2.7810	0.1288	0.1293	320
9	26	2.6254	2.6380	0.1451	0.1437	322
10	30.	2.3265	2.3344	0.1848	0.1835	331
11	19	2.1097	2.1035	0.2247	0.2260	217
12	23	2.0357	2.0404	0.2413	0.2402	108
13	8.3	1.9602	1.9672	0.2602	0.2584	510
14	8.6	1.7506	1.7453	0.3265	0.3283	426
15	7.2	1.6772	1.6718	0.3555	0.3578	600
16	4.9	1.5776	1.5788	0.4018	0.4012	601
17	6.2	1.5639	1.5665	0.4089	0.4075	540
18	7.1	1.4570	1.4580	0.4711	0.4704	339
19	6.0	1.3475	1.3492	0.5507	0.5493	722
20	6.8	1.3142	1.3170	0.5790	0.5765	730

compound crystallizes in a tetragonal system with lattice parameters: a = 10.03; c = 16.67 Å, z = 7, $\rho_{pycn.}$ = 5.72 g/cm^3, $\rho_{X\text{-}ray}$ = 5.75 g/cm^3. Crystallographic data of $Cr_2Sb_2S_3Te_3$ compound are shown in Table 2.

4. Conclusions

Thus, the Sb_2S_3–Cr_2Te_3 system was studied using physicochemical analysis methods and its phase diagram was constructed. It was established that the Sb_2S_3–Cr_2Te_3 section is a quasi-binary

section of eutectic type. A quaternary compound $Cr_2Sb_2S_3Te_3$ is formed in the system with an anion exchange of components in the ratio of 1:1. The $Cr_2Sb_2S_3Te_3$ compound is formed by the peritectic reaction M + Cr_2Te_3 ↔ $Cr_2Sb_2S_3Te_3$ at 610 °C. The eutectic with a composition of 20 mol. % Cr_2Te_3 is formed in the system between the α phase and $Cr_2Sb_2S_3Te_3$ at a temperature of 430 °C. In the Sb_2S_3 based system solid solutions reached up to 5 mol. % Cr_2Te_3, and in the system based on Cr_2Te_3 it was up to 8 mol. % Sb_2S_3. Based on the results of X-ray phase analysis, it was established that the $Cr_2Sb_2S_3Te_3$ compound crystallizes in a tetragonal system with lattice parameters: A = 10.03; c = 16.67 Å, z = 7, density $\rho_{pycn.}$ = 5.72 g/cm^3, $\rho_{X\text{-}ray}$ = 5.5 g/cm^3.

Author contributions

Aliev I. I. – writing the article and scientific supervision of research; Mamedov E. I. – idea for scientific work and writing the article; Yusubov F. V. – scientific editing of the text, final conclusions; Masieva L. F. – conducting research; Gashimov Kh. M – conducting research.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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