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Phase Equilibrium in the $AgInSe_2$-CdSe System

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Results of phase equilibrium in the $AgInSe_2$–CdSe system by differential thermal, X-ray, microstructural analyses and measurements of microhardness are given. The system is quasibinary with limited solubility of the components in the solid state. The region of solid solution on the base of $AgInSe_2$ is 4 mol.% CdSe (820 K). The ranges of solid solutions on the base of CdSe are much larger (up to 40 mol.% $AgInSe_2$ at 820 K). Coordinates of eutectic point are 10 mol.% CdSe, 1023 K. The alloy $AgCd_2InSe_4$ is located in the solid solution ranges based on CdSe.

Key words: quasibinary system, solid solution, phase diagram, differential thermal analysis

$AgInSe_2$–CdSe system is formed by semiconductors, which exhibit some interesting physical properties, making them perspective for technical use. Silver-indium selenide draws particular attention because of the possibility to make on its basis luminodiodes of linearly polarized light and phototransformers of sun radiation with a high efficiency. Cadmium selenide is used as photoelectrical material. Though initial $AgInSe_2$ and CdSe compounds were investigated rather intensively, T-x phase diagram of the $AgInSe_2$–CdSe system is not known. Only [1] is known for synthesis of a tetragonal compound of $AgCd_2InSe_4$ composition to which the authors ascribe wurtzite structure (space group $P6_3mc$, $a = 0.4277$ nm, $c = 0.6988$ nm). In [2] the melting point (1273 K) is determined and investigation of physical properties of the alloy $AgCd_2InSe_4$ are given. $AgInSe_2$ is known to melt congruently at 1067 K, and at 976 K it undergoes polymorphic transformation [3]. Low temperature modification is crystallized in the chalcopyrite structure, space group $I\bar{4}2d$, with the parameters of lattice $a = 0.60905$ nm, $c = 1.1583$ nm [3]. At high pressure and temperature $AgInSe_2$ exists in various crystal structures: cubic, type NaCl, and type ZnS [4]. Cadmium selenide melts congruently at 1512 K [5]. CdSe exists in two polymorphic modifications: metastable cubic, type α-ZnS, and stable wurtzite modification (β-ZnS). The transition sphalerite ⇔ wurtzite is observed after 10-hour annealing of the sample at 403 K. Complete transformation of cubic modification into hexagonal, with the lattice parameters $a = 0.429$ nm, $c = 0.700$ nm, is observed after 18-hour annealing at 973 K [6].

EXPERIMENTAL

Samples for investigation were prepared from pure elements (Se 99.997 wt.%, In 99.999 wt.%, Cd 99.9999 wt.% and Ag 99.999 wt.%) using the method of high temperature synthesis in evacuated to 0.1 Pa quartz ampoules. Maximum temperature of the synthesis was 1273 K, at which the samples were kept during 4 hours, with the following cooling up to 820 K. At this temperature annealing during 300 hours was made, which was followed by hardening the samples in the saturated solution NaCl at room temperature. Survey of the diffractograms of the alloys belonging to the system under investigation was made on X-ray apparatus DRON-4-13 (CuKα-radiation, Ni-filter). The results of the survey were treated by the program PD Win-2. The results of X-ray analyses were confirmed by the data of microstructural investigations and measurements of microhardness. The ground edges of the samples were etched by chromic mixture during 10–30 min. Microhardness of the phases was measured at loading 0.196 H. Differential thermal analysis was made on the installation consisting of the furnace of regulated heating "Thermodent" (it's maximal temperature of heating was 1420 K) and x-y self-recorder type H 307/1. The temperature measurement was made by Pt/Pt-Rh thermocouple, heating and cooling of the furnace was performed with the rate 11 K/min.

RESULTS AND DISCUSSION

The system was found to be quasibinary with limited solubility of the components in the solid state. The region of solid solution on the base of silver-indium selenide is small, up to 4 mol.% CdSe (820 K), at the change of lattice parameters from a = 0.61024(3) nm, c = 1.1709(1) nm for chalcopyrite modification $AgInSe_2$ to a = 0.60969(4) nm, c = 1.1753(2) nm for the alloy of composition 95 mol.% $AgInSe_2$ × 5 mol.% CdSe (Fig. 1). The ranges of solid solutions on the base of cadmium selenide are much larger (up to 40 mol.% $AgInSe_2$ at 820 K), that was determined on the base of the change of unit cell parameters from a = 0.42994(1) nm, c = 0.7010(2) nm for

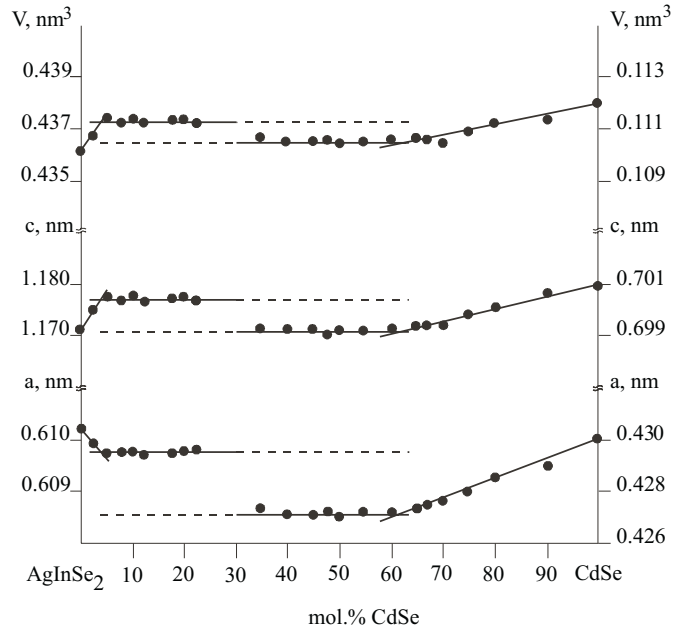

Figure 1. Changes of crystal lattices parameters in the $AgInSe_2$–CdSe system for the temperature 820 K.

wurtzite modification CdSe to a = 0.42712(3) nm, c = 0.6993(1) nm for the alloy of the composition 40 mol.% $AgInSe_2$ × 60 mol.% CdSe (Fig. 1).

The results of the measurements are shown in Table 1. As it is seen, microhardness within the range of solid solutions on the base $AgInSe_2$ and, especially, CdSe increases markedly relative to the microhardness of the initial components.

Table 1. Alloy compositions and corresponding values of microhardness.

№	Composition of charge, mol.% $AgInSe_2$	Phase composition of the samples	Microhardness (kg/mm^2)
1	100	α	190(α)
2	97.5	α	212(α)
3	95	α + γ	217(α)
4	92.5	α + γ	–
5	90	α + γ	–
6	88	α + γ	223(α)
7	85	α + γ	220(α)
8	83	α + γ	220(α)
9	80	α + γ	–
10	78	α + γ	–
11	75	α + γ	–
12	70	α + γ	–
13	65	α + γ	–
14	63	α + γ	–
15	60	α + γ	273(γ)
16	55	α + γ	273(γ)
17	53	α + γ	269(γ)
18	50	α + γ	273(γ)
19	45	α + γ	273(γ)
20	40	α + γ	–
21	35	γ	230(γ)
22	33.3	γ	235(γ)
23	30	γ	241(γ)
24	25	γ	–
25	20	γ	202(γ)
26	10	γ	181(γ)
27	5	γ	149(γ)
28	CdSe	γ	105(γ)

Thermogram of $AgInSe_2$ shows two endothermal effects: at 963 K and 1060 K, which agree with the literature data [3]. The first of them corresponds to cation-cation disorder (transition chalcopyrite ⇔ sphalerite), the second effect – to melting temperature. Thermograms of the alloys with composition 90–100 mol.% CdSe do not show any thermal effect, as the maximum temperature to which the samples could be heated was 1420 K and, apparently, temperatures of liquidus and solidus were higher (Table 2).

Table 2. DTA results of the alloys of the $AgInSe_2$–CdSe system.

№	Phase composition, (mol.%)		Thermal effects (K)		
	$AgInSe_2$	CdSe	liquidus	solidus	hard phase transformation
1	100	0	1060	–	963
2	97.5	2.5	1043	1029	1043
3	95	5	1041	1027	1046
4	92.5	7.5	1028	–	1042
5	90	10	1039	1027	1001,982,934,885
6	88	12	1045	–	961,899
7	85	15	1053	–	936,893
8	83	17	1059	1025	909
9	80	20	1080	1025	–
10	78	22	1083	1017	899
11	75	25	1093	1020	898
12	70	30	1111	1035	–
13	65	35	1129	1083	–
14	63	37	1133	1115	–
15	60	40	1143	1111	–
16	55	45	1158	1133	–
17	53	47	1170	1133	–
18	50	50	1184	1153	–
19	45	55	1211	1173	–
20	40	60	1237	1213	–
21	35	65	1267	1233	–
22	33.3	66.7	1275	1243	
23	30	70	1295	1273	–
24	25	75	1325	–	–
25	20	80	1348	–	–
26	10	90	–	–	–
27	5	95	–	–	–
28	0	100	–	–	–

According to differential thermal, X-ray, microstructural analyses and measurements of microhardness, the phase diagram of the $AgInSe_2$–CdSe system was given (Fig. 2). Coordinates of eutectic point "b": 10 mol.% CdSe, 1023 K. At this temperature γ-solid solutions have the largest extent, with the decreasing of temperature the solubility decreases and at annealing temperature (820 K) it equals 60 mol.% CdSe. The solubility on the base of high temperature modification of $AgInSe_2$ (β-solid solution) is 5 mol.% CdSe at eutectic temperature, and it increases with decreasing temperature to 17 mol.% CdSe. As it is seen from Fig. 2, at 898 K the β-solid solution decomposes by the eutectoid process $\beta \Leftrightarrow \alpha + \gamma$. At the same temperature the α-solid solution has the largest extent – up to 12 mol.% CdSe. With decreasing temperature the extent of α-solid solutions decreases.

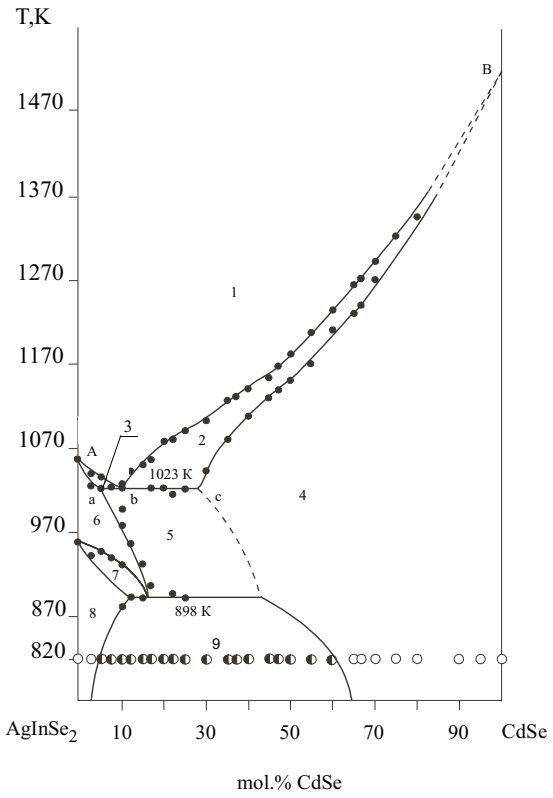

Figure 2. Phase diagram of $AgInSe_2$–CdSe system: 1 – L, 2 – L + γ, 3 – L + β, 4 – γ, 5 – β + γ, 6 – β, 7 – β + α, 8 – α, 9 – α + γ, ❍ – monophase field, ◑– diphase field.

The $AgCd_2InSe_4$ compound, described in [1,2], does not exist according to data of this paper, *i.e*. the alloy of the $AgCd_2InSe_4$ composition corresponds to the solid solution ranges of CdSe. As to the melting temperature of the alloy (1275 K) that corresponds to the composition, it correlated with the literature data [2].

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