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Phase diagrams of the $AgIn_5Se_8$–$AgGaSe_2$ and $AgIn_5Se_8$–Ga_2Se_3 systems of the quasi-ternary system Ag_2Se–Ga_2Se_3–In_2Se_3

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Using X-ray diffraction, differential-thermal and microstructural analyses and microhardness measurements, the quasi-binary systems $AgIn_5Se_8$–$AgGaSe_2$ and $AgIn_5Se_8$–Ga_2Se_3 were investigated. Based on the results of the research, their phase diagrams were constructed.

X-ray phase analysis / Differential-thermal analysis / Microstructural analysis / Microhardness / Phase diagram

Introduction

Investigation of the $AgIn_5Se_8$–$AgGaSe_2$ and $AgIn_5Se_8$–Ga_2Se_3 systems is a necessary step in the study of the quasiternary system Ag_2Se–Ga_2Se_3–In_2Se_3. These systems may form large areas of solid solutions based on binary and ternary compounds, which can be used in semiconductor devices.

The Ag_2Se–In_2Se_3 system features one compound, $AgIn_5Se_8$, which melts congruently at 1088 K. Its high-temperature modification crystallizes with tetragonal symmetry, space group (S.G.) *P*-42*m*, lattice parameters a = 0.57934(4) nm, c = 1.16223(2) nm [1]. The microhardness of $AgIn_5Se_8$ is 3.5±0.01 GPa [2]. The Ag_2Se–Ga_2Se_3 system also features one compound, $AgGaSe_2$, which melts congruently at 1123 K and crystallizes with tetragonal symmetry, S.G. *I*-42*m*, lattice parameters a = 0.5992(5) nm, c = 1.0886(1) nm [3]. The microhardness of $AgIn_5Se_8$ is 4.4±0.01 GPa [4]. The Ga–Se system features a compound, Ga_2Se_3, that melts congruently at 1293 K and crystallizes with cubic symmetry, S.G. *F*-43*m*, unit cell parameter a = 0.5429(4) nm [5]. The microhardness of Ga_2Se_3 is 3.5±0.01 GPa [6]. According to the literature data, all these compounds melt congruently, crystallize in the tetragonal or cubic system, and form solid solution ranges.

Experimental

Using the direct single-temperature method, 21 alloys of the $AgIn_5Se_8$–$AgGaSe_2$ and $AgIn_5Se_8$–Ga_2Se_3 systems were synthesized in evacuated quartz ampoules at 1150 K or 1290 K (depending on the composition) from high-purity elements: Ag – 99.99 wt.%, Ga, In – 99.999 wt.% and Se – 99.9999 wt.%. The alloys were investigated by X-ray diffraction analysis (XRD), which was performed using a DRON 4-13 diffractometer with Cu K_α-radiation (scan step 0.05°, exposure time 2 s), microstructure analysis (MSA) and microhardness measurements, using a Leica VMHT Auto microhardness tester. Differential thermal analysis (DTA) was performed using a device composed of a THERMODENT regulated heating furnace, an H-207 XY-recorder and a Pt-Pt/Rh thermocouple.

Results

Based on the XRD (Fig. 1) and DTA results, the phase diagram of the $AgIn_5Se_8$–$AgGaSe_2$ system was constructed. It belongs to the Roozeboom type V (Fig. 2). It contains an α-solid solution range of the high-temperature modification (HTM) of $AgIn_5Se_8$ and a β-solid solution range of $AgGaSe_2$. The lattice parameters (Fig. 3) in the $AgIn_5Se_8$ homogeneity region change from a = 0.57994(2) nm, c = 1.1622(1) nm for the compound $AgIn_5Se_8$ to a = 0.57767(2) nm, c = 1.1563(1) nm for the sample of composition 30 mol.% $AgGaSe_2$ – 70 mol.% $AgIn_5Se_8$. The lattice parameter a in the $AgGaSe_2$ homogeneity region decreases from 0.59807(4) nm to 0.57789(3) nm, and the lattice parameter c increases from 1.0804(3) nm to 1.1427(1) nm, while the tetrahedral distortion of the unit cell, $\delta = 2\text{-}c/a$, decreases from 0.194 to 0.023. This is due to the replacement of Ga^{3+} ($r(Ga^{3+})$ = 0.062 nm [6]) by larger In^{3+} ($r(In^{3+})$=0.076 nm [6]), which leads to cell lengthening along the direction c. The XRD results

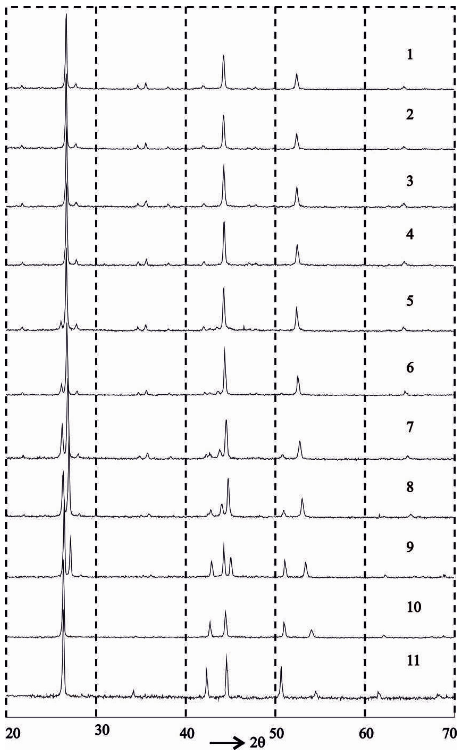

Fig. 1 X-ray powder diffraction diagrams of the samples of the $AgIn_5Se_8$−$AgGaSe_2$ system annealed at 820 K:
(1) 100 mol.% $AgIn_5Se_8$;
(2) 90 mol.% $AgIn_5Se_8$–10 mol.% $AgGaSe_2$;
(3) 80 mol.% $AgIn_5Se_8$–20 mol.% $AgGaSe_2$;
(4) 70 mol.% $AgIn_5Se_8$–30 mol.% $AgGaSe_2$;
(5) 60 mol.% $AgIn_5Se_8$–40 mol.% $AgGaSe_2$;
(6) 50 mol.% $AgIn_5Se_8$–50 mol.% $AgGaSe_2$;
(7) 40 mol.% $AgIn_5Se_8$–60 mol.% $AgGaSe_2$;
(8) 30 mol.% $AgIn_5Se_8$–70 mol.% $AgGaSe_2$;
(9) 20 mol.% $AgIn_5Se_8$–80 mol.% $AgGaSe_2$;
(10) 10 mol.% $AgIn_5Se_8$–90 mol.% $AgGaSe_2$;
(11) 100 mol.% $AgGaSe_2$.

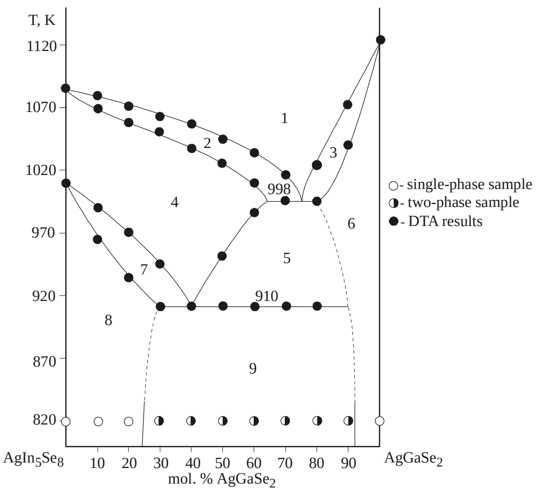

Fig. 2 Phase diagram of the $AgIn_5Se_8$−$AgGaSe_2$ system: (1) L; (2) L+α; (3) L+β; (4) α; (5) α+β; (6) β; (7) α+α'; (8) α'; (9) α'+β.

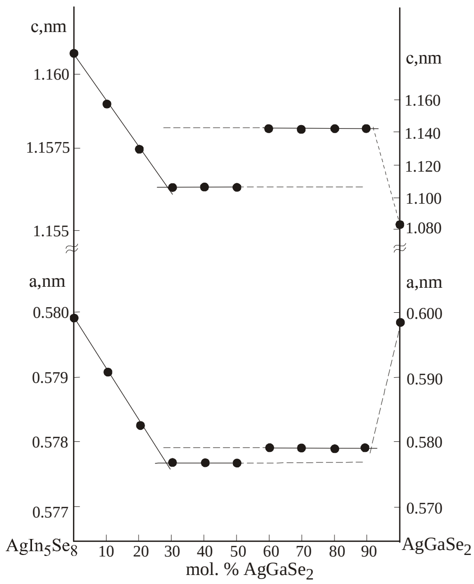

Fig. 3 Lattice parameters of the samples of the $AgIn_5Se_8$−$AgGaSe_2$ system.

were confirmed by MSA and microhardness measurements (Table 1).

There is a eutectic point L↔α+β in the system with the coordinates 75 mol.% $AgGaSe_2$ – 25 mol.% HT-$AgIn_5Se_8$, 998 K. The extent of the α-solid solution range at the eutectic temperature is 64 mol.% $AgGaSe_2$, that of the β-solid solution range is 20 mol.% $AgIn_5Se_8$. There is eutectoid dissolution of the α-solid solution, α↔ α'+β at 910 K, where α' is the solid solution of the low-temperature modification (LTM) of $AgIn_5Se_8$; the eutectoid point corresponds to a composition of 60 mol.% $AgIn_5Se_8$ – 40 mol.% $AgGaSe_2$. The extent of the α'-solid solution range decreases from 30 mol.% $AgGaSe_2$ at the eutectoid temperature to 25 mol.% $AgGaSe_2$ at 820 K. The extent of the β-solid solution range varies from 10 to 8 mol.% $AgIn_5Se_8$ with decreasing temperature.

Diffraction patterns of the alloys in the $AgIn_5Se_8$–Ga_2Se_3 system are plotted in Fig. 4. An α'-solid solution range of HT-$AgIn_5Se_8$ and a γ-solid solution range of Ga_2Se_3 form in this system. The lattice parameters in the α'-solid solution range change from a = 0.57994(2) nm, c = 1.1622(1) nm for $AgIn_5Se_8$ to a = 0.56922(3) nm, c = 1.1421(2) nm for the sample of composition 50 mol.% $AgIn_5Se_8$ – 50 mol.% Ga_2Se_3. The lattice parameters in the γ-solid solution range change from a = 0.5423(4) nm for Ga_2Se_3 to a = 0.55793(2) nm for the sample of composition 80 mol.% Ga_2Se_3 – 20 mol.% $AgIn_5Se_8$ (Fig. 5). The XRD results were confirmed by MSA and microhardness measurements (Table 2).

Based on the XRD and DTA results, the phase diagram of the $AgIn_5Se_8$–Ga_2Se_3 system, which belongs to type IV of Roozeboom's classification, was constructed (Fig. 6). There is a peritectic process L+γ↔α at 1115 K. The coordinates of the peritectic

Table 1 Microhardness and phase composition of the alloys of the $AgIn_5Se_8$−$AgGaSe_2$ system.

No.	Nominal composition of the sample	Phase composition	Microhardness, GPa±0.01	
1	100 mol.% $AgIn_5Se_8$	α	3.20	–
2	90 mol.% $AgIn_5Se_8$–10 mol.% $AgGaSe_2$	α	3.25	–
3	80 mol.% $AgIn_5Se_8$–20 mol.% $AgGaSe_2$	α	3.35	–
4	70 mol.% $AgIn_5Se_8$–30 mol.% $AgGaSe_2$	α+β	(α) 3.48	(β) 3.88
5	60 mol.% $AgIn_5Se_8$–40 mol.% $AgGaSe_2$	α+β	(α) 3.49	(β) 3.89
6	50 mol.% $AgIn_5Se_8$–50 mol.% $AgGaSe_2$	α+β	(α) 3.49	(β) 3.89
7	40 mol.% $AgIn_5Se_8$–60 mol.% $AgGaSe_2$	α+β	(α) 3.50	(β) 3.90
8	30 mol.% $AgIn_5Se_8$–70 mol.% $AgGaSe_2$	α+β	(α) 3.49	(β) 3.92
9	20 mol.% $AgIn_5Se_8$–80 mol.% $AgGaSe_2$	α+β	(α) 3.49	(β) 3.95
10	10 mol.% $AgIn_5Se_8$–90 mol.% $AgGaSe_2$	α+β	(α) 3.51	4.15
11	100 mol.% $AgGaSe_2$	β	–	4.40

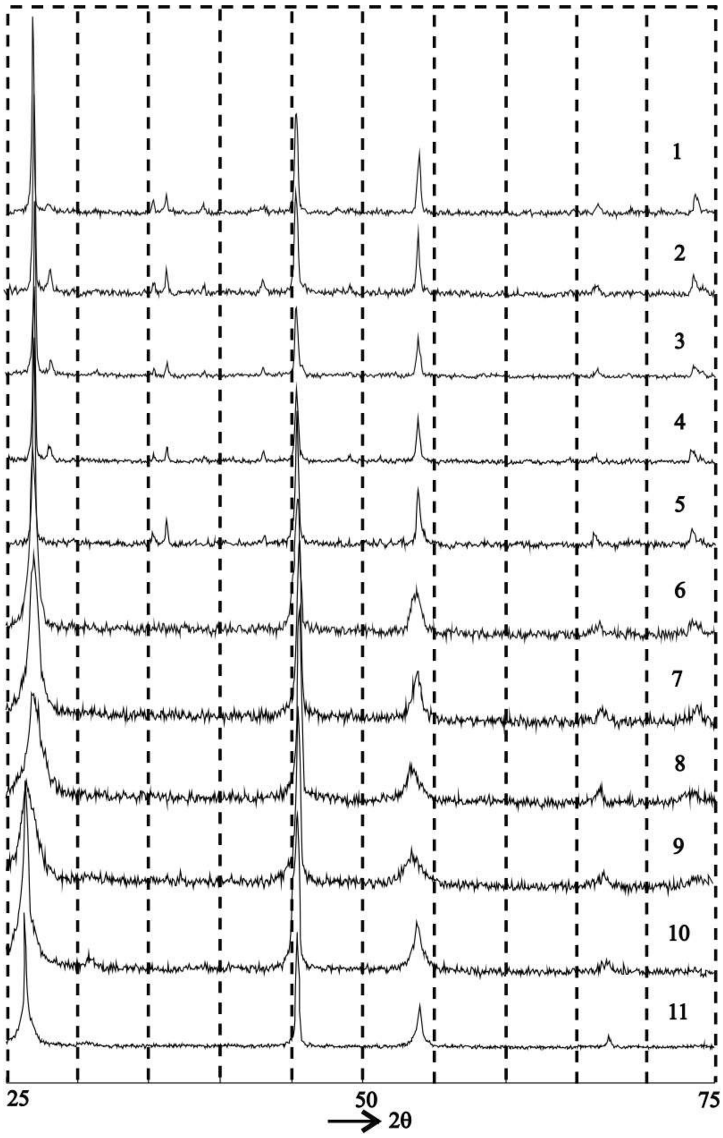

Fig. 4 X-ray powder diffraction diagrams of the samples in the $AgIn_5Se_8$−Ga_2Se_3 system annealed at 820 K: (1) 100 mol.% $AgIn_5Se_8$; (2) 80 mol.% $AgIn_5Se_8$–20 mol.% Ga_2Se_3; (3) 60 mol.% $AgIn_5Se_8$–40 mol.% Ga_2Se_3; (4) 50 mol.% $AgIn_5Se_8$–50 mol.% Ga_2Se_3; (5) 40 mol.% $AgIn_5Se_8$–60 mol.% Ga_2Se_3; (6) 30 mol.% $AgIn_5Se_8$–70 mol.% Ga_2Se_3; (7) 20 mol.% $AgIn_5Se_8$–80 mol.% Ga_2Se_3; (8) 15 mol.% $AgIn_5Se_8$–85 mol.% Ga_2Se_3; (9) 10 mol.% $AgIn_5Se_8$–90 mol.% Ga_2Se_3;(10) 2 mol.% $AgIn_5Se_8$–98 mol.% Ga_2Se_3; (11) 100 % Ga_2Se_3.

Table 2 Microhardness and phase composition of the alloys of the $AgIn_5Se_8$−Ga_2Se_3 system.

No.	Nominal composition of the sample	Phase composition	Microhardness, GPa±0.01	
1	100 mol.% $AgIn_5Se_8$	α	3.20	–
2	80 mol.% $AgIn_5Se_8$–20 mol.% Ga_2Se_3	α	2.40	–
3	60 mol.% $AgIn_5Se_8$–40 mol.% Ga_2Se_3	α	1.70	–
4	50 mol.% $AgIn_5Se_8$–50 mol.% Ga_2Se_3	α+γ	(α) 1.44	(γ) 2.29
5	40 mol.% $AgIn_5Se_8$–60 mol.% Ga_2Se_3	α+ γ	(α) 1.46	(γ) 2.31
6	30 mol.% $AgIn_5Se_8$–70 mol.% Ga_2Se_3	α+ γ	(α) 1.45	(γ) 2.28
7	20 мол. % $AgIn_5Se_8$–80 mol.% Ga_2Se_3	α+ γ	(α) 1.48	(γ) 2.27
8	15 mol.% $AgIn_5Se_8$–85mol.% Ga_2Se_3	γ	–	2.35
9	10 mol.% $AgIn_5Se_8$–90 mol.% Ga_2Se_3	γ	–	2.45
10	2 mol.% $AgIn_5Se_8$–98 mol.% Ga_2Se_3	γ	–	2.55
11	100 mol.% Ga_2Se_3	γ	–	3.00

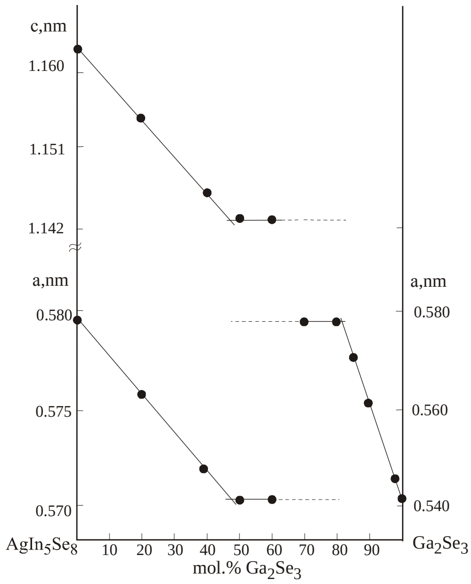

Fig. 5 Lattice parameters of the samples of the $AgIn_5Se_8$−Ga_2Se_3 system.

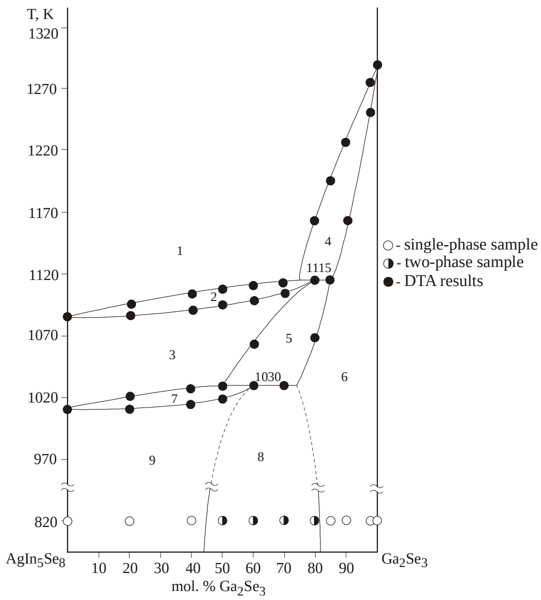

Fig. 6 Phase diagram of the $AgIn_5Se_8$−Ga_2Se_3 system: (1) L; (2) L+α; (3) α; (4) L+γ; (5) α+γ; (6) γ; (7) α+α'; (8) α'+γ; (9) α'.

point are 75 mol.% Ga_2Se_3, 1115 K. At this temperature the extent of the α-solid solution range is 80 mol.% $AgGaSe_2$, that of the γ-solid solution range is 15 mol.% $AgIn_5Se_8$. The peritectoid interaction of the α- and γ-solid solutions α+γ↔ α' takes place at 1030 K, with a coordinate of 50 mol.% Ga_2Se_3 for the peritectoid point. The extent of the α'-solid solution range is 45 mol.% Ga_2Se_3 at 820 K. At the same temperature the γ-solid solution extends to 18 mol.% $AgIn_5Se_8$.

The phase diagrams of the $AgIn_5Se_8$–$AgGaSe_2$ and $AgIn_5Se_8$–Ga_2Se_3 systems were constructed. They belong to type V and type IV of Roozeboom's classification, respectively, and reveal the formation of large solid solutions ranges, which may serve as new semiconductor materials.

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