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The $AgGaSe_2$+SnS_2 Û $AgGaS_2$+$SnSe_2$ System

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The reciprocal system $AgGaSe_2 + SnS_2 \Leftrightarrow AgGaS_2 + SnSe_2$ was investigated by physico-chemical analysis methods. The liquidus surface projection, the isothermal section at 720 K, and three vertical sections were constructed. The system liquidus consists of two fields of the primary crystallization. The existence of α- and β-solid solutions with the tetragonal and the monoclinic structure, respectively, was established. The system does not have a stable diagonal, therefore it is classified as a reversible reciprocal system.

Key words: phase diagram, solid solutions, lattice parameters.

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Introduction

The $A^IB^{III}C_2^{VI}$ compounds are widely used in non-linear optics [1-4]. The goal of the increase of the transparency region and of the double-refraction angle brings to attention the investigation of the $A^IB^{III}C_2^{VI}$ – $D^{IV}C_2^{VI}$ systems [5–8]. An additional characteristic of interest of the $AgGaS_2$ and $AgGaSe_2$ compounds is that the dispersion curves of the refraction indices $n_e(\lambda)$ and $n_o(\lambda)$ cross at the wavelengths 4974 and 8100 Å, respectively. It is expected that as sulfur is substituted with selenium, and silver and gallium are substituted with tin, the isotropic point will shift to the long-wave region, and the restructuring will thus cover a wide spectral range [9].

The literature has no reports on the investigation of phase equilibria in the $AgGaSe_2 + SnS_2 \Leftrightarrow AgGaS_2 + SnSe_2$ system, therefore the objective of this paper is the study of the phase diagram and the boundaries of the solid solution ranges of the system components to estimate the feasibility of obtaining new materials for non-linear optics.

According to the data of [10,11] $AgGaS_2$ and $AgGaSe_2$ melt congruently at 1268 and 1124 K respectively. Silver thiogallate crystallizes in the tetragonal symmetry, space group (S.G.) *I`42d;* $a$ = 0.57572 nm, $c$ = 1.03036 nm [12]. Silver selenogallate is isostructural with the thiogallate (S.G.) *I`42d*; a = 0.5992 nm, c=1.0880 nm [13]. According to [14,15], SnS_2 and $SnSe_2$ melt congruently at 1143 and 898 K respectively. Tin diselenide crystallizes in the monoclinic symmetry, S.G. *P`3m1*; $a$ = 0.3811 nm, $c$= 0.6137 nm [16]. Tin disulfide also crystallizes in the monoclinic symmetry, S.G. *P`3m1*; a = 0.3646 nm, c = 0.5879 nm [14]. The systems $AgGaS_2$ – $AgGaSe_2$ [17] and SnS_2 – $SnSe_2$ [18] which are the boundary sides of the reciprocal system are characterized by the continuous solubility in both liquid and solid state. The $AgGaS_2$ – SnS_2 and $AgGaSe_2$ – $SnSe_2$ systems are of the eutectic type, with the eutectic point coordinates 59 mol.% SnS_2, 994 K and 71 mol.% $SnSe_2$, 843 K, respectively. The solid solution ranges of $AgGaS_2$ and $AgGaSe_2$ at 720 K contain 13 mol.% SnS_2 or 26 mol.% $SnSe_2$, respectively [19]. The solid solubility in SnS_2 or $SnSe_2$ is negligible.

I. Experimental

The investigation of the phase equilibria in the $AgGaSe_2 + SnS_2 \Leftrightarrow AgGaS_2 + SnSe_2$ system was based on 51 alloys. Their compositions were located at the $AgGaSe_2$ – SnS_2, $AgGaS_2$ – $SnSe_2$, and AgGaSSe–SnSSe sections. The alloys were synthesized by the two-temperature method in evacuated to 0.1 Pa quartz ampoules using vibration mixing. The batches were composed of high-purity elements (purity of Ag 99.997 wt.%, Ga 99.997 wt.%, Sn 99.99 wt.%, Se 99.997 wt.%, S 99.9997 wt.%). The maximum synthesis temperature was 1370 K. The $AgGaS_2$- and $AgGaSe_2$-rich alloys increase in volume upon cooling [20] and crack the ampoules, therefore double quartz containers were used to avoid oxidation after cracking. Obtained alloys were annealed at 720 K for 480 hours followed by quenching into cold water.

The alloys were investigated by differential thermal,

X-ray phase and microstructure analysis. Differential thermal analysis was performed using a VDTA-8M3 derivatograph, with In, Sn, Zn, Al, NaCl, Ge, Ag, Cu, Fe as reference points, and tungsten as the standard. The heating and cooling rates were 10 K/min. Temperature was controlled by a W-Re 0.05/W-Re 0.2 thermocouple. X-ray phase analysis was performed using a DRON 4-13 diffractometer, Cu K_α radiation. Microstructure analysis utilized a Leica VMHT Auto microhardness tester.

II. Results and discussion

The vertical section $AgGaS_2$ – $SnSe_2$ of the ternary reciprocal system $AgGaSe_2 + SnS_2 \Leftrightarrow AgGaS_2 + SnSe_2$ is presented in Fig. 1. It forms one of the diagonals of the concentration quadrangle. The system liquidus consists

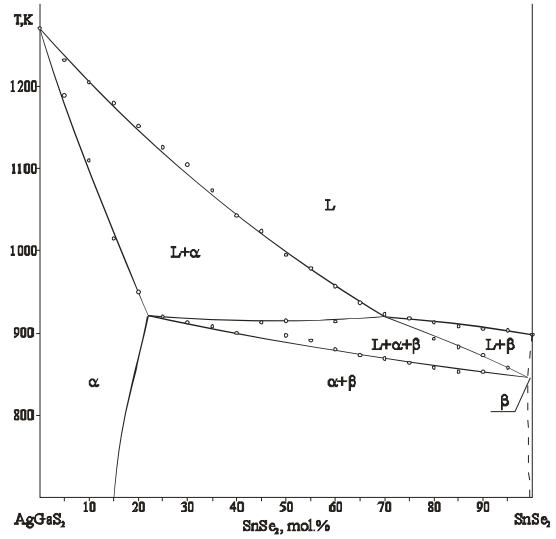

Fig. 1. Vertical section of the $AgGaS_2$ – $SnSe_2$ system.

of two fields that correspond to the primary crystallization of the solid solution ranges of $AgGaS_2$ and $SnSe_2$. The sub-liquidus part, in addition to the fields of the primary crystallization of these solid solutions, contains the three-phase field of the secondary crystallization of the binary eutectic $L \Leftrightarrow \alpha + \beta$. The line of the completion of the secondary crystallization, together with those of the boundary solid solutions, form the section solidus. The maximum extent of α-solid solution range of $AgGaS_2$ is 22 mol.% $SnSe_2$ which decreases to 15 mol.% $SnSe_2$ with the temperature decrease to 720 K. The change of the lattice parameters within the range of α-solid solutions which crystallize in the tetragonal symmetry is plotted in Fig. 2. The solid solubility in $SnSe_2$ is negligible according to XRD (Fig. 3) and microstructure analysis data. The β-solid solutions crystallize in the monoclinic symmetry. The change of the unit cell parameters and the shift of the positions of major reflections in the two-phase region indicate that

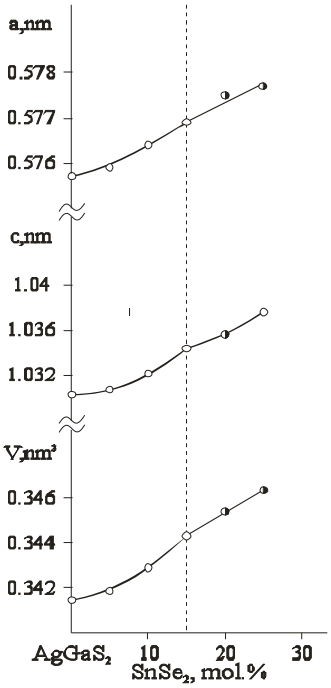

Fig. 2. Change of the unit cell parameters of the solid solutions of the $AgGaS_2$ – $SnSe_2$ section.

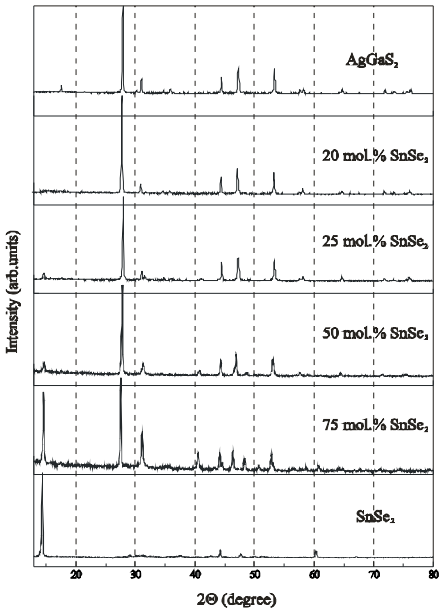

Fig. 3. Diffraction patterns of the alloys of the $AgGaS_2$ – $SnSe_2$ section.

the $AgGaS_2 - SnSe_2$ section is non-quasi-binary at the annealing temperature.

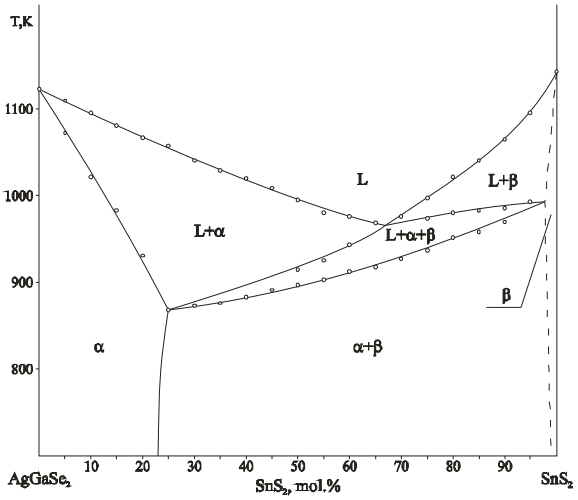

Fig. 4. Vertical section of the $AgGaSe_2 - SnS_2$ system.

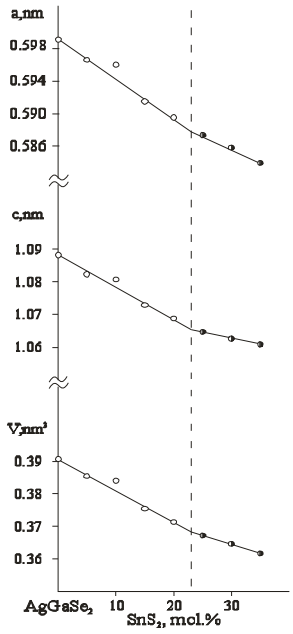

Fig. 5. Change of the unit cell parameters of the solid solutions of the $AgGaSe_2 - SnS_2$ section.

The vertical section $AgGaSe_2 - SnS_2$ is shown in Fig. 4. It makes the other diagonal of the $AgGaSe_2 + SnS_2 \Leftrightarrow AgGaS_2 + SnSe_2$ system. The system liquidus consists of two fields of the primary crystallization of the solid solution ranges of $AgGaSe_2$ and SnS_2. The sub-liquidus part consists of the fields of the primary crystallization of α-solid solution range of $AgGaSe_2$ and β-solid solution range of SnS_2, and a three-phase field $L \Leftrightarrow \alpha + \beta$. The maximum extent of α-solid solution range of $AgGaSe_2$ which crystallize in the tetragonal symmetry is 25 mol.% SnS_2 at 868 K which decreases to 23 mol.% SnS_2 with the temperature decrease to 720 K. The change of the lattice parameters within α-solid solution range is plotted in Fig. 5; their change in the two-phase region indicates that the section is non-quasi-binary. The results of XRD and microstructure analysis show negligible solid solubility in SnS_2.

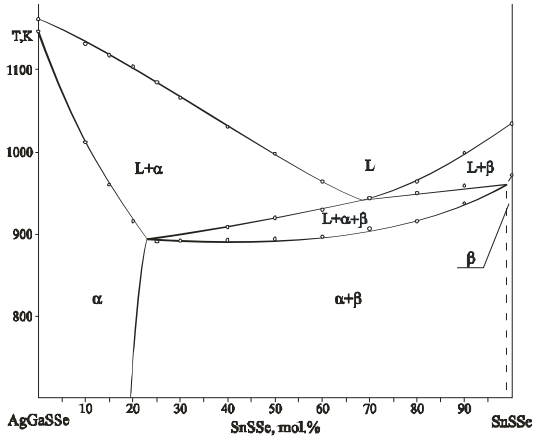

Fig. 6. Vertical section of the AgGaSSe – SnSSe system.

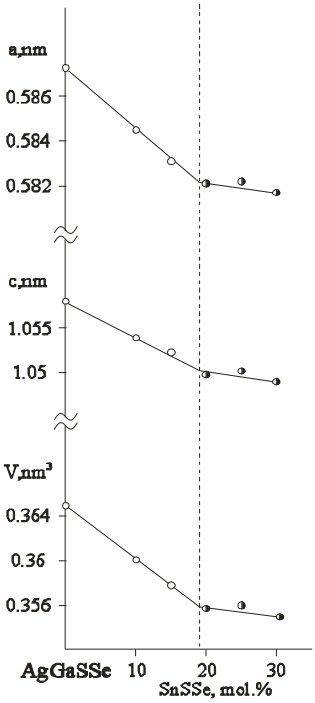

Fig. 7. Change of the unit cell parameters of the solid solutions of the AgGaSSe – SnSSe section.

The vertical section 'AgGaSSe' – 'SnSSe' is shown in Fig. 6. It was investigated to refine the liquidus surface projection and the isothermal section of the reciprocal system. The diagram is similar to the two previous ones. The maximum extent of α-solid solution range is 23 mol.% SnS_2 at 893 K; this decreases to 19 mol.% SnS_2 as the temperature decreases to 720 K. A gradual slope of the curve of the change of the lattice parameters in the two-phase region (Fig. 7) indicates that this section is

non-quasi-binary.

Projection of the liquidus surface and the isothermal section at 720 K of the $AgGaSe_2 + SnS_2 \Leftrightarrow AgGaS_2 + SnSe_2$ system.

The liquidus surface projection of the $AgGaSe_2 + SnS_2 \Leftrightarrow AgGaS_2 + SnSe_2$ system (Fig. 8) was constructed

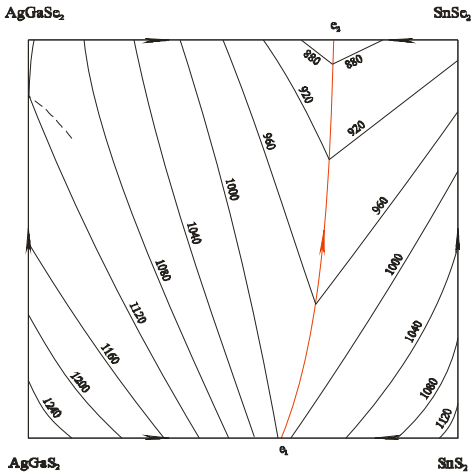

Fig. 8. Liquidus surface projection of the $AgGaSe_2 + SnS_2 \Leftrightarrow AgGaS_2 + SnSe_2$ system.

using the literature data on the systems $AgGaS_2 – AgGaSe_2$ [17], $SnS_2 – SnSe_2$ [18], $AgGaS(Se)_2 – SnS(Se)_2$ [19] and the presented results of the investigation of three vertical sections. The projection consists of two fields of the primary crystallization of α- and β-solid solutions of the ternary silver-gallium chalcogenides and of the binary tin chalcogenides, respectively. The larger part of the concentration quadrangle is occupied by the field of the primary crystallization of α-solid solutions as this phase has the highest melting point in the system. The fields of the primary crystallization are separated by a mono-variant line e_1e_2 which corresponds to the secondary crystallization of the binary eutectic L⇔α+β; the temperature decreases from e_1 to e_2.

The isothermal section of the reciprocal system $AgGaSe_2 + SnS_2 \Leftrightarrow AgGaS_2 + SnSe_2$ (Fig. 9) contains two single-phase regions of the solid solutions which are

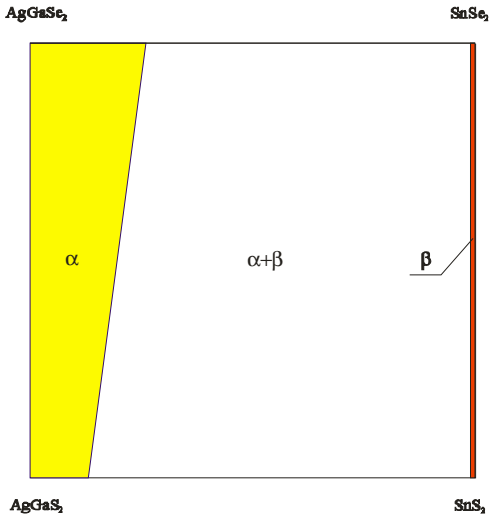

Fig. 9. The isothermal section of the $AgGaSe_2 + SnS_2 \Leftrightarrow AgGaS_2 + SnSe_2$ system at 720 K.

stretched along the sides $AgGaS_2 – AgGaSe_2$ and $SnS_2 – SnSe_2$ of the quadrangle.

The absence of a stable diagonal in the $AgGaSe_2 + SnS_2 \Leftrightarrow AgGaS_2 + SnSe_2$ system classifies it, according to the criteria of [21], as a reversible reciprocal system.

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Система $AgGaSe_2+SnS_2$ Û $AgGaS_2+SnSe_2$

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Досліджено систему $AgGaSe_2 + SnS_2 \Leftrightarrow AgGaS_2 + SnSe_2$. Побудовано проекцію поверхні ліквідуса, ізотермічний переріз при 720 K та три політермічні перерізи. Ліквідус системи складається із двох полів первинної кристалізації α– і β– твердих розчинів, які кристалізуються в тетрагональній та моноклінній сингонії відповідно. У системі відсутня стабільна діагональ, що відносить її до взаємних зворотніх систем.

Ключові слова: діаграма стану, тверді розчини, параметри гратки.