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SOLID-PHASE EQUILIBRIA IN THE RECIPROCAL SYSTEM **I.J. Alverdiyev***Ganja State University**ialverdiyev73@gmail.com*

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Solid-state equilibria at 800 and 300 K in the $6\text{Ag}_2\text{S} + \text{Ag}_8\text{SnSe}_6 \leftrightarrow 6\text{Ag}_2\text{Se} + \text{Ag}_8\text{SnS}_6$ system which is of interest from the point of view of obtaining new mixed ion-electron conductors were studied by DTA, XRD and SEM methods. According to the results obtained it was shown that the system is reversibly reciprocal and is characterized by the formation of continuous (800 K) or wide (300 K) regions of substitutional solid solutions along the boundary systems $\text{Ag}_2\text{S}-\text{Ag}_2\text{Se}$ and $\text{Ag}_8\text{SnS}_6-\text{Ag}_8\text{SnSe}_6$.

Keywords: *Ag-Sn-S-Se system, silver chalcostannates, phase diagram, $\text{Ag}_8\text{SnS}_6-\text{Ag}_8\text{SnSe}_6$ section, solid solutions.*

doi:**Introduction**

In recent years, complex chalcogenides based on copper and silver have been given great attention as environmentally friendly functional materials with thermoelectric and other properties [1–9]. This makes them promising for use in alternative energy devices and other functional areas of high technology. According to available data, many of these compounds have high ionic conductivity $\text{Cu}^+(\text{Ag}^+)$ and can be used as photoelectrode materials, electrochemical converters of solar energy, ion-selective sensors, photoelectrochemical visualizers, ionistors, etc. [10–15].

Among the most intensively studied such materials, silver chalcostannates and phases based on them can be noted [16–21]. According to the authors of these works, the presence of mixed electron-ion conductivity is one of the significant factors that positively affect their thermoelectric characteristics.

At the initial stage of the development of new multicomponent materials, the study of phase equilibria and thermodynamic properties of the corresponding systems is important [22–25]. Similar data sets for complex chalcogenides of copper and silver were obtained in [26–33].

This paper presents the results of a study of solid-state equilibria in the $6\text{Ag}_2\text{S} + \text{Ag}_8\text{SnSe}_6 \leftrightarrow 6\text{Ag}_2\text{Se} + \text{Ag}_8\text{SnS}_6$ reciprocal system. This system is an independent part of the reciprocal system $2\text{Ag}_2\text{S} + \text{SnSe}_2 \leftrightarrow 2\text{Ag}_2\text{Se} + \text{SnS}_2$, which is

of interest from the point of view of obtaining anion-substituted solid solutions based on silver chalcostannates.

Three of the four quasibinary boundary components – $\text{Ag}_2\text{S}-\text{Ag}_8\text{SnS}_6$, $\text{Ag}_2\text{Se}-\text{Ag}_8\text{SnS}_6$ and $\text{Ag}_2\text{S}-\text{Ag}_2\text{Se}$ of the investigated system, were studied in detail [34–37]. The first two are of the eutectic type [34, 35], and the third is characterized by the formation of a continuous series of high-temperature solid solutions [36]. According to [37] at temperatures below 390 K in the $\text{Ag}_2\text{S}-\text{Ag}_2\text{Se}$ system, an intermediate phase of variable composition (ϵ) as well as limited solid solutions based on low-temperature modifications of the starting compounds (α_1 and α_2) are formed.

A feature of all the starting compounds of the $6\text{Ag}_2\text{S} + \text{Ag}_8\text{SnSe}_6 \leftrightarrow 6\text{Ag}_2\text{Se} + \text{Ag}_8\text{SnS}_6$ system is the presence of polymorphic transitions at relatively low temperatures [5, 34, 35]. This allows us to expect a change in the character of solid-phase equilibria in a studied system with temperature.

Experimental part**Synthesis**

The synthesis of the starting compounds was carried out by direct interaction of elementary components of a high degree of purity in evacuated ($\sim 10^{-2}$ Pa) quartz ampoules in a dual-zone inclined furnace. The lower "hot" zone was heated to temperatures 30–50⁰ – above the

melting point of the synthesized compound, and the upper "cold" zone was 650 K (for sulfides) or 900 K (for selenides) [38]. In such temperature regimes, for two hours, chalcogen completely interacts with metal components, as evidenced by the absence of traces of chalcogen (dark vapor phase and drops) on the inner walls of the ampoule.

All synthesized compounds were identified by differential-thermal analysis (DTA), powder X-ray diffraction method (PXRD) and scanning electron microscopy (SEM).

Alloys of the boundary system Ag_8SnS_6 – Ag_8SnSe_6 and inside the concentration plane $6\text{Ag}_2\text{S} + \text{Ag}_8\text{SnSe}_6 \leftrightarrow 6\text{Ag}_2\text{Se} + \text{Ag}_8\text{SnS}_6$ (each weighing 0.5 g) were prepared by fusion of the starting compounds in various ratios in evacuated quartz tubes. After melting, the temperature was lowered to 800 K, at which thermal annealing was performed for 500 hours. A number of alloys after annealing were quenched in cold water.

Analysis

DTA, XRD and SEM techniques were employed to check the purity of the synthesized starting compounds and analyze the samples.

DTA was performed using a NETZSCH 404 F1 Pegasus differential scanning calorime-

ter. Heating rate was of 10 K/min and accuracy about $\pm 2^\circ$.

X-ray powder diffraction data were collected at room temperature using a Bruker D8 ADVANCE powder diffractometer utilizing CuK_α –radiation within $2\theta = 10$ to 70° . The unit cell parameters were calculated by indexing of powder patterns using Topas V3.0 software.

The microstructure and equilibrium compositions of the phases were determined by FEI Quanta™ 250 scanning electron microscope.

Results

Powder X-ray diffraction patterns of alloys of the Ag_8SnS_6 – Ag_8SnSe_6 system, slowly cooled after annealing, are shown in Figure 1. As can be seen, alloys with compositions of 40–100 mol% Ag_8SnSe_6 have diffraction patterns qualitatively similar to the diffraction pattern of the low-temperature orthorhombic modification of Ag_8SnSe_6 (δ_2 -phase) (Table). An alloy with a composition of 20 mol% Ag_8SnSe_6 is also single-phase and its diffraction pattern is similar to the diffraction pattern of pure Ag_8SnS_6 (low-temperature modification). The diffraction pattern of the 30 mol% Ag_8SnSe_6 alloy consists of a set of reflection lines of δ_1 - and δ_2 - phases.

Fig. 1. Powder XRD patterns for some compositions in the Ag_8SnS_6 – Ag_8SnSe_6 system.

The XRD results of alloys quenched after annealing at 800 K showed that they are all single-phase and have diffraction patterns characteristic of cubic syngony.

The crystallographic data of δ_1 , δ_2 , and δ -phases are presented in Table. The period of the cubic lattice of high-temperature δ -solid solutions has a linear dependence on the composition, i.e. obeys Vegard's rule.

The XRD results were confirmed by SEM (Figure 2). As can be seen, alloys with compositions of 20 and 40 mol% Ag_8SnSe_6 are single-phase, while the alloy with a composition of 30 mol% Ag_8SnSe_6 is two-phase.

The results of SEM and XRD analysis of selected alloys of the $6\text{Ag}_2\text{S}+\text{Ag}_8\text{SnSe}_6 \leftrightarrow 6\text{Ag}_2\text{Se}+\text{Ag}_8\text{SnS}_6$ system, quenched after annealing at 800 K, showed that they are all two-phase and consist of a mixture of α - and δ -phases. The symbol α refers to a continuous series of solid solutions of the $\text{Ag}_2\text{S}-\text{Ag}_2\text{Se}$ boundary system. According to these data, the solid-phase diagram of the reciprocal system

$6\text{Ag}_2\text{S}+\text{Ag}_8\text{SnSe}_6 \leftrightarrow 6\text{Se}+\text{Ag}_8\text{SnS}_6$ at 800 K has been constructed (Figure 3a).

The character of solid-phase equilibria in this system at room temperature (Figure 3b) differs sharply from Figure 3a. As can be seen from Figure 3b at 300K, this system consists of a two-phase ($\alpha_1+\delta_1$, $\alpha_2+\delta_1$, $\alpha_2+\delta_2$) and three-phase ($\alpha_1+\alpha_2+\delta_1$, $\alpha_2+\delta_1+\delta_2$) fields. The formation of these phase regions is caused by solid-phase transformations in the boundary systems $\text{Ag}_2\text{S}-\text{Ag}_2\text{Se}$ and $\text{Ag}_8\text{SnS}_6-\text{Ag}_8\text{SnSe}_6$. Our data indirectly indicate that the intermediate ε -phase does not exist in the boundary system $\text{Ag}_2\text{S}-\text{Ag}_2\text{Se}$ system. And the region of homogeneity of the α_2 phase is much wider than indicated in [37] and covers the composition range of 45–100 mol% Ag_2Se . According to Figure 4, the diffraction pattern of alloy #1 consists of the reflection lines of α_2 - and δ_2 -phases. If a two-phase region $\alpha_2+\varepsilon$ existed in the boundary system, this would lead to the formation of a three-phase region $\alpha_2+\delta_2+\varepsilon$ and alloy #1 would be in this phase region.

Types and crystal parameters of solid solutions of the $\text{Ag}_8\text{SnS}_6-\text{Ag}_8\text{SnSe}_6$ system

Composition, mol% Ag_8SnSe_6	Syngony, Sp.Gr., crystal parameters, Å			
	Room temperature			Quenched at 900 K
	Orthorhombic			Cubic, F-34m
	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>
0 (Ag_8SnS_6)	15.334	7.562	10.724	10.858
20	15.425	7.618	10.795	10.911
40	7.769	7.656	10.823	10.953
60	7.819	7.712	10.898	11.018
80	7.865	7.768	10.973	11.073
100	7.913	7.825	11.047	11.122

Fig. 2. SEM images for some alloys in the $\text{Ag}_8\text{SnS}_6-\text{Ag}_8\text{SnSe}_6$ system: 20 mol% Ag_8SnSe_6 (a); 30 mol% Ag_8SnSe_6 (b); 40 mol% Ag_8SnSe_6 (c).

Fig. 3. Solid-phase diagram of the $6\text{Ag}_2\text{S} + \text{Ag}_8\text{SnSe}_6 \leftrightarrow 6\text{Se} + \text{Ag}_8\text{SnSe}_6$ system at 800 K (a) and 300 K (b). #1 – alloy, XRD of which is shown in Figure 4.

Fig. 4. Powder diffraction pattern of alloy #1 which is shown in Figure 3.

Conclusion

We have constructed solid-phase equilibrium diagrams of the $6\text{Ag}_2\text{S}+\text{Ag}_8\text{SnSe}_6\leftrightarrow 6\text{Ag}_2\text{Se}+\text{Ag}_8\text{SnS}_6$ system at 800 and 300 K. It is shown that this reciprocal system is adiabatic. At 800 K, it is characterized by the formation of continuous areas of substitution solutions along boundary systems $\text{Ag}_2\text{S}-\text{Ag}_2\text{Se}$ and $\text{Ag}_8\text{SnS}_6-\text{Ag}_8\text{SnSe}_6$. At 300 K it is characterized by a more complex interaction leading to the formation of a number of two- and three phase regions. Obtained solid solutions based on both modifications of the starting compounds are of practical interest as functional materials with mixed ion-electron conductivity.

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6Ag₂S+Ag₈SnSe₆↔6Ag₂Se+Ag₈SnS₆ QARŞILIQLI SISTEMİNDƏ BƏRKFAZA TARAZLIQLARI

İ.C.Alverdiyev

DTA, RFA və SEM üsulları ilə qarışıq ion-elektron keçiricilərinin alınması baxımından maraq kəsb edən $6Ag_2S + Ag_8SnSe_6 \leftrightarrow 6Ag_2Se + Ag_8SnS_6$ sisteminə 800 və 300 K temperaturalarda bərkfaza tarazlıqları öyrənilmişdir. Müəyyən edilmişdir ki, sistem qarşılıqlı dönər olub, $Ag_2S - Ag_2Se$ və $Ag_8SnS_6 - Ag_8SnSe_6$ sistemləri boyunca fasiləsiz (800 K) və ya geniş (300 K) bərk məhlul sahələri əmələ gəlməsi ilə xarakterizə olunur.

Açar sözlər: Ag–Sn–S–Se sistemi, gümüş xalkostannatları, faza diaqramı, $Ag_8SnS_6 - Ag_8SnSe_6$ kəsiyi, bərk məhlullar.

ТВЕРДОФАЗНЫЕ РАВНОВЕСИЯ ВО ВЗАИМНОЙ СИСТЕМЕ $6Ag_2S + Ag_8SnSe_6 \leftrightarrow 6Ag_2Se + Ag_8SnS_6$

И.Дж.Алвердиев

Методами ДТА, РФА и СЭМ изучены твердофазные равновесия в при 800 и 300 К в системе $6Ag_2S + Ag_8SnSe_6 \leftrightarrow 6Ag_2Se + Ag_8SnS_6$, которая представляет интерес с точки зрения получения новых смешанных ионно-электронных проводников. На основании полученных данных показано, что система взаимно-обратимая и характеризуется образованием непрерывных (800 К) или широких полей (300 К) твердых растворов замещения вдоль граничных систем $Ag_2S - Ag_2Se$ и $Ag_8SnS_6 - Ag_8SnSe_6$.

Ключевые слова: система Ag–Sn–S–Se, халкостаннаты серебра, фазовая диаграмма, разрез $Ag_8SnS_6 - Ag_8SnSe_6$, твердые растворы.