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PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

Interactions in the $Sn_2Sb_6S_{11}$–$PbSnSb_4S_8$ System

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Abstract—The $Sn_2Sb_6S_{11}$–$PbSnSb_4S_8$ system was studied by physicochemical analysis methods (differential thermal, X-ray powder diffraction, and microstructural analyses and microhardness and density measurements). It was found that this system is a quasi-binary section of the SnS–PbS–Sb_2S_3 ternary system of the eutectic type. The coordinates of the eutectic are 42 mol % $PbSnSb_4S_8$ and 600 K. In the studied system, regions of solid solutions were detected, which extend for solid solutions based on $Sn_2Sb_6S_{11}$ to 4 mol % $PbSnSb_4S_8$ (α) and for solid solutions based on $PbSnSb_4S_8$ to 6 mol % $Sn_2Sb_6S_{11}$ (β).

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One of the modern efforts of searching for new materials with controlled properties is to synthesize and grow single crystals of multicomponent chalcogenide semiconductors.

Therefore, the development of a scientifically grounded technology for synthesizing chalcogenides, especially sulfides, is of high importance. Sulfides of germanium and arsenic group elements, in particular, SnS, PbS, and Sb_2S_3 are promising thermoelectric and photosensitive materials [1–5].

In view of the practical value of materials based on chalcogenides of tin, lead, and arsenic, it is necessary to gain a deeper insight into their interaction. For understanding the interaction between $Sn_2Sb_6S_{11}$ and $PbSnSb_4S_8$, and also for searching for new compounds and solid solutions, the $Sn_2Sb_6S_{11}$–$PbSnSb_4S_8$ system was studied.

The compound $Sn_2Sb_6S_{11}$ melts congruently at 750 K and crystallizes in the rhombic system [6]. According to our previous data [7, 8], $PbSnSb_4S_8$ melts at 825 K and crystallizes in the rhombic system with the unit cell parameters a = 21.68 Å, b = 7.47 Å, c = 4.12 Å, space group *Pbmm*, and Z = 2 [7].

EXPERIMENTAL

Quaternary alloys for investigation were synthesized in evacuated quartz ampules from binary sulfides at 800–880 K. Binary sulfides PbS, SnS, and Sb_2S_3 were produced from elemental substances of special purity grade. With increasing SnS content above 80 mol %, iron-gray splintery layered substances were obtained.

The alloys were studied by X-ray powder diffraction analysis (DRON-2 diffractometer, CuK_α radiation, Ni filter), differential thermal analysis (NTR-70 device), microstructural analysis (MIM-7 microscope), and microhardness (RMT-3 microhardness tester) and density measurements.

RESULTS AND DISCVUSSION

To investigate the phase equilibrium in the $Sn_2Sb_6S_{11}$–$PbSnSb_4S_8$ system, 14 samples of various compositions were synthesized (Table 1). Alloys in the system are air- and water-resistant, soluble in mineral acids (H_2SO_4, HNO_3, HCl), and insoluble in organic solvents.

Figure 1 presents the state diagram of the $Sn_2Sb_6S_{11}$–$PbSnSb_4S_8$ section, which shows that the section is a quasi-binary section of the SnS–PbS–Sb_2S_3 ternary system, and the state diagram of this system is of the eutectic type. The eutectic has the coordinates 42 mol % $PbSnSb_4S_8$ and 600 K.

The liquidus of the system consists of the primary crystallization branches of α-solid solutions based on $Sn_2Sb_6S_{11}$ and β-solid solutions based on $PbSnSb_4S_8$.

Investigation of the microstructure of the alloys showed that, near the $Sn_2Sb_6S_{11}$ and $PbSnSb_4S_8$ points, there are limited regions of solubility. To determine the boundaries of the regions of solid solutions, we additionally synthesized alloys containing 98, 97, 95, 93, and 90 mol % of the initial components. The obtained alloys were annealed at 550 and 400 K for 180 h and then quenched (Table 2).

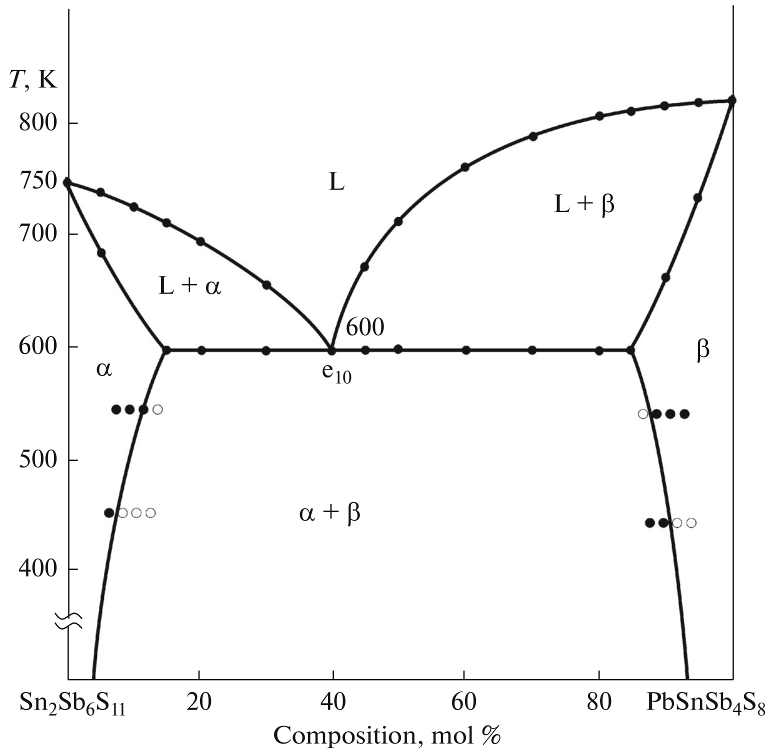

Fig. 1. Phase diagram of the $Sn_2Sb_6S_{11}$–$PbSnSb_4S_8$ system.

The boundary composition of the homogeneity region based on $Sn_2Sb_6S_{11}$ at the eutectic temperature is 18 mol %, and the solubility limit at room temperature is 4 mol % $PbSnSb_4S_8$. The solid solutions based on $PbSnSb_4S_8$ at the eutectic temperature (600 K) reach 16 mol %. With decreasing temperature, the solubility limit decreases and is 6 mol % at room temperature. These solutions crystallize in the rhombic system. With increasing $Sn_2Sb_6S_{11}$ content, the unit cell parameters of these solutions increase (a = 21.68–21.74 Å, b = 7.47–7.53 Å, c = 4.12–4.17 Å) (Table 3), and in the heterogeneous region the reflections in the X-ray powder diffraction pattern remain almost unchanged.

Within the concentration range 0–4 mol % $PbSnSb_4S_8$, the X-ray powder diffraction patterns exhibit only the diffraction lines of $Sn_2Sb_6S_{11}$; within the range 4–94 mol % $PbSnSb_4S_8$, the lines of α-solid solutions based on $Sn_2Sb_6S_{11}$ and β-solid solutions based on $PbSnSb_4S_8$; and within the range 94–100 mol % $PbSnSb_4S_8$, only the diffraction lines of $PbSnSb_4S_8$, which confirm the formation of β-solid solutions on its basis.

Table 1. Compositions, differential thermal analysis data, and microhardness measurements of alloys in the $Sn_2Sb_6S_{11}$–$PbSnSb_4S_8$ system

Composition, mol %		Temperature of event, K	Microhardness, MPa	Composition, mol %		Temperature of event, K	Microhardness, MPa
$Sn_2Sb_6S_{11}$	$PbSnSb_4S_8$			$Sn_2Sb_6S_{11}$	$PbSnSb_4S_8$		
100	0.0	750	910	50	50	600, 635	1750
95	5.0	675, 740	980	40	60	600, 690	1750
90	10	600, 725	980	30	70	600, 725	1750
80	20	600, 700	980	20	80	600, 760	1750
70	30	600, 665	980	10	90	790	1750
60	40	600, 615	980	5.0	95	725, 810	1720
58	42	600 (eut)	Eutectic	0.0	100	825	1650

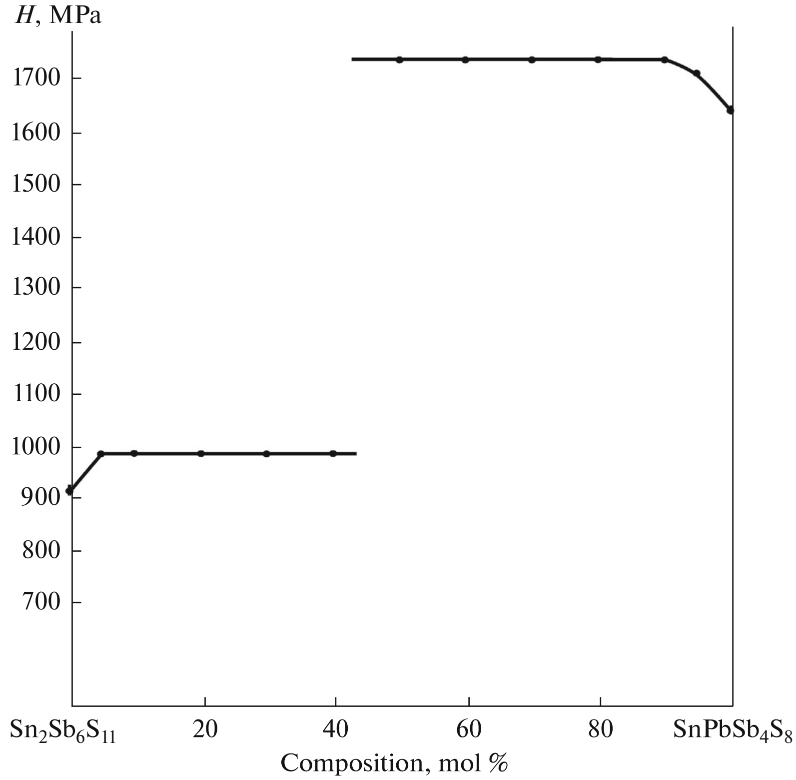

Fig. 2. Microhardness versus $Sn_2Sb_6S_{11}$ content of $PbSnSb_4S_8$.

Measurements of the microhardness of the alloys demonstrated that, in the section, two sets of values, 910–980 and 1650–1750 MPa, are observed, which characterize α- and β-solid solutions based on $Sn_2Sb_6S_{11}$ and $PbSnSb_4S_8$, respectively. With increasing content of the second component, the microhardness increases, and in the heterogeneous region, the microhardness remains virtually constant (Fig. 2).

Single crystals for structural and optical measurements were grown by directional crystallization.

To grow single crystals of $(PbSnSb_4S_8)_{1-x}(Sn_2Sb_6S_{11})_x$, polycrystalline alloys were preliminarily synthesized in an amount of 7–10 g, which were then ground and transferred into an ampule with a tapered bottom. The ampule was evacuated and placed in a two-temperature furnace with a preset temperature gradient. The electric furnace moved at a velocity of 3 mm/h, whereas the ampule remained immobile [8]. Such a design allowed one to remove interference caused by the shaking of the ampule. During repeated experiments, the temperatures of furnace zones and the furnace velocity were refined (Table 4). As a result, single crystals suitable for further investigations were obtained.

It was determined that the $Sn_2Sb_6S_{11}$–$PbSnSb_4S_8$ system is a quasi-binary section and is of the eutectic type with limited solubility based on the initial components.

Thus, in this work:

(1) For the first time, the state diagrams of the $Sn_2Sb_6S_{11}$–$PbSnSb_4S_8$ section were constructed. It was found that the $Sn_2Sb_6S_{11}$–$PbSnSb_4S_8$ section is a

Table 2. Results of microstructural analysis of alloys in the $Sn_2Sb_6S_{11}$–$PbSnSb_4S_8$ system after annealing at 400 and 550 K

Composition, mol %		Number of phases at annealing temperature, K	
$Sn_2Sb_6S_{11}$	$PbSnSb_4S_8$	400	550
98	2.0	One	One
97	3.0	Two	One
95	5.0	Two	One
93	7.0	Two	Two
90	10	Two	Two
2.0	98	One	One
3.0	97	One	One
5.0	95	Two	One
7.0	93	Two	One
10	90	Two	Two

Table 3. Crystallographic and some physicochemical data on solid solutions in the $Sn_2Sb_6S_{11}$–$PbSnSb_4S_8$ system

Composition, mol % $Sn_2Sb_6S_{11}$	Unit cell parameter, Å			Space group	*Z*	Micro-hardness, MPa	Density, g/cm^3	
	a	*b*	*c*				exp.	calcd.
0.0	21.68	7.47	4.12	*Pbmm*	2	1650	5.33	5.35
1.0	21.70	7.47	4.13	*Pbmm*	2	1680	5.36	5.37
3.0	21.72	7.50	4.15	*Pbmm*	2	1690	5.38	5.39
4.0	21.74	7.53	4.17	*Pbmm*	2	1710	5.40	5.42

Table 4. Optimal conditions for growing single crystals of solid solutions $(PbSnSb_4S_8)_{1-x}(Sn_2Sb_6S_{11})_x$

Composition of single crystal	*T*, K	Furnace velocity, mm/h	Weight of single crystal, g	Size of single crystal, mm
$(PbSnSb_4S_8)_{0.992}(Sn_2Sb_6S_{11})_{0.008}$	700–850	3.5	6.5	8 × 20
$(PbSnSb_4S_8)_{0.96}(Sn_2Sb_6S_{11})_{0.04}$	700–850	3.0	6.7	8 × 20
$(PbSnSb_4S_8)_{0.94}(Sn_2Sb_6S_{11})_{0.06}$	700–850	3.0	6.8	8 × 20
$(PbSnSb_4S_8)_{0.92}(Sn_2Sb_6S_{11})_{0.08}$	700–850	3.0	6.6	8 × 20

quasi-binary section of the SnS–Sb_2S_3–PbS quasi-ternary system of the eutectic type.

(2) In the $Sn_2Sb_6S_{11}$–$PbSnSb_4S_8$ section at room temperature, regions of solid solutions form: solid solutions based on $Sn_2Sb_6S_{11}$ extend to 4 mol % $PbSnSb_4S_8$ (α), and solid solutions based on $PbSnSb_4S_8$ reach 6 mol % $Sn_2Sb_6S_{11}$ (β).

(3) In the $Sn_2Sb_6S_{11}$–$PbSnSb_4S_8$ section, single crystals of solid solutions based on $PbSnSb_4S_8$ were grown by the Bridgman–Stockbarger method.

(4) According to the results of studying the temperature dependences of some electrophysical parameters of the compound $PbSnSb_4S_8$ and the solid solution $(PbSnSb_4S_8)_{1-x}(Sn_2Sb_6S_{11})_x$, the alloys are *p*-type semiconductors.

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