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THE Bi_2S_3 – YbS SYSTEM

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Abstract: *The phase equilibrium in the Bi_2S_3 – YbS system was studied by the methods of physicochemical analysis – DTA, XRD, MSA through measuring the micro-hardness and density, and a state diagram was plotted. It has been found that this system is a quasi-binary cross-section of the Yb-Bi-S ternary system. The formation of the two ternary compounds with $YbBi_2S_4$ and $YbBi_4S_7$ compositions was detected and the areas of solid solutions determined.*

Keywords*: system, eutectic, congruent, incongruent, state diagram, Bi_2S_3, YbS*
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Introduction

The obtaining of new promising materials with optical and thermoelectric properties is of great importance. One of the ways to obtain functional materials is to study phase equilibria in the systems based on already known binary compounds. Accordingly, the study of the Bi_2S_3-YbS system is of both scientific and practical interest due the starting, since the binary compounds have unique semiconductor properties [1-7].

The YbS compound melts congruently at 2403K and crystallizes in a cubic crystal system with lattice parameters of unit cell: a = 5.694 Å, the type of structure NaCl (space group Fm3m) [8].

Bi_2S_3 compound - melts congruently at 1048K and has a rhombic lattice of the Sb_2S_3 type with parameters: a = 11.15 Å; b = 11.29 Å; c = 3.98 Å [9-11].

The purpose of this work is to plot a phase diagram of the state of Bi_2S_3 – YbS and study the physicochemical properties of the new discovered phases.

Experimental part

The study of the Bi_2S_3 – YbS system was carried out by methods of physicochemical analysis: differential thermal (DTA), X-ray diffraction (XRD), micro-structural (MSA) analyses, as well as by measuring the density and microhardness. The DTA curves have been recorded using an NTR-72 and "Termoskon 2" thermographs. Al_2O_3 was used as an etalon; the heating rate was 10^0/min. Diffraction patterns were recorded on a "D2 PHASER" X-ray diffractometer with CuK_α radiation and a Ni filter. The micro-hardness was determined using a "Thixomet Smart Drive" micro-hardness tester at loads selected as a result of the micro-hardness studies into each phase. The MSA of the polished etched thin sections was studied using an MIM microscope. The etchant was a chromium mixture ($K_2Cr_2O_7$+concentrated H_2SO_4):H_2O=1:1.

Alloys of the Bi_2S_3 – YbS system were synthesized both from the initial materials and the binary components of Bi_2S_3 and YbS. Elements were used for the synthesis of the alloys: Bi (B-4); Yb-ITM-1 (individual total more than 1) S-EC (sulfur extra clean). The samples were alloyed in sealed quartz ampoules, previously evacuated to a residual pressure of 10 Pa, in the temperature range 900-1500K. In order to obtain an equilibrium state, the homogenization annealing was performed at

600-800 K for 700 h, depending on the composition.

Results and discussion

The state diagram of the Bi_2S_3 – YbS system was plotted due to the results of the study. It was found that two ternary compounds have been formed in this system. The Bi_2S_3 – YbS system is quasi-binary and has a complex character (Fig. 1).

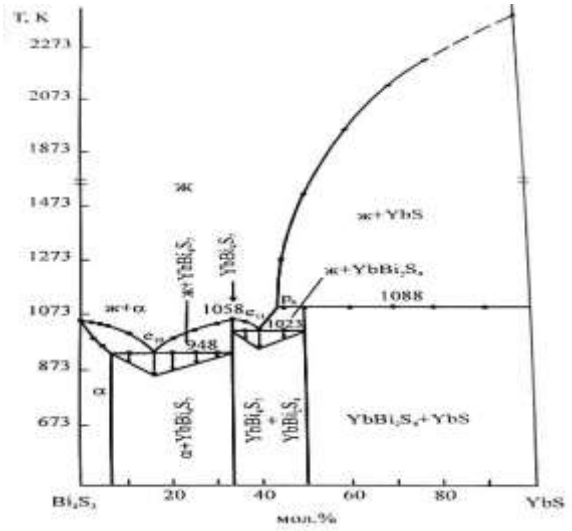

Figure 1. The state diagram of the cross section of Bi_2S_3 – YbS

The liquidus of the Bi_2S_3 – YbS system consists of branches of the primary crystallization of phases: α- phase based on Bi_2S_3, $YbBi_4S_7$, $YbBi_2S_4$ and YbS compounds. The coordinates of the eutectic points between Bi_2S_3 and $YbBi_4S_7$ are as follows: 18 mol% YbS and 948K, and between $YbBi_4S_7$ and $YbBi_2S_4$ 40 mol% YbS and 1023K. The Bi_2S_3 – YbS system can be conditionally represented as two subordinate systems: Bi_2S_3 - $YbBi_4S_7$ and $YbBi_4S_7$ - YbS. The first subsystem belongs to the eutectic type. In the second subsystem, the $YbBi_2S_4$ ternary compound has formed according to the peritectic reaction. The liquidus of primary crystallization was roughly plotted in the concentration range of 8-100 mol% YbS. Nonvariant points of the Bi_2S_3-YbS system are shown in Table 1.

Table 1. Nonvariant points of the Bi_2S_3-YbS system

T.K.	Bi_2S_3 mol%	Solid phase	Feature of the point
948	85	Bi_2S_3 – $YbBi_4S_7$	eutectic
1058	66.7	$YbBi_4S_7$	dystectic
1023	60	$YbBi_4S_7$ – $YbBi_2S_4$	eutectic
1088	50	$YbBi_2S_4$	peritectic

According to the DTA data, microstructural and X-ray diffraction analyses and the formation of two $YbBi_2S_4$ and $YbBi_4S_7$ compounds were established (Table 1). The $YbBi_2S_4$ compound melts incongruently at a temperature of 1088 K and is formed by the peretectic reaction: liq. + YbS $YbBi_2S_4$. The $YbBi_4S_7$ compound melts congruently at 1058K.

According to the XRD data, in the concentration range 5-33.3 mol% of YbS, α (solid solutions based on Bi_2S_3) and $YbBi_4S_7$ co-crystallize, in the concentration range 33.3 mol% of YbS, $YbBi_4S_7$ and $YbBi_2S_4$ co-

crystallize, and in the concentration range 50-100 mol% of YbS, $YbBi_2S_4$ and YbS co-crystallize. Solid solutions based on bismuth sesqui-sulphide are locate in the concentration range of 0-5 mol% YbS at a room temperature, while at a eutectic temperature (948K) - in 8 mol% YbS. Solubility based on ytterbium monosulfide was not established.

Table 2. Interplanar distances of Bi_2S_3, $YbBi_4S_7$, $YbBi_2S_4$ and YbS

Bi_2S_3		$YbBi_4S_7$		$YbBi_2S_4$		YbS	
d_{exp}	I/I_0	d_{exp}	I/I_0	d_{exp}	I/I_0	d_{exp}	I/I_0
6.650	20	5.6348	67	5.5928	39	6.5886	12
5.040	19	5.0246	30	4.9139	30	3.8557	8
3.970	38	3.9868	37	3.9576	34	3.2350	90
3.750	20	3.6972	17	3.6515	14	2.8302	100
3.560	94	3.5516	100	3.5516	100	1.9626	90
3.530	60	3.3663	12	3.3513	15	1.7108	53
3.256	18	3.2226	10	3.2457	18	1.6342	35
3.118	100	2.9895	59	3.0910	51		
2.811	63	2.7956	20	2.8565	19		
2.716	34	2.6907	12	2.7888	15		
2.641	24	2.6292	10	2.7388	6		
2.520	35	2.5064	36	2.6492	11		
2.499	13	2.4546	13	2.5064	15		
2.456	15	2.3516	12	2.4481	8		
2.304	24	2.2475	33	2.3028	8		
2.256	36	2.1697	7	2.2675	45		
2.129	9	2.0790	13	2.1467	8		
2.118	15	1.9795	10	2.0974	11		
2.096	11	1.8929	20	1.9804	23		
2.074	10	1.8716	27	1.9434	27		
1.990	33	1.8424	7	1.8788	6		
1.953	55	1.6979	19	1.8537	8		
1.935	20	1.6760	7	1.6955	23		
1.915	20	1.6240	6				
1.884	14	1.5491	7				
1.854	17						

According to the microstructural analysis, alloys containing 0-5; 33.3 m 50 mol% YbS are single phased. The formation of two ternary compounds in the system was also confirmed by plotting the dependence of H_μ on composition X (Fig. 2).

The $YbBi_4S_7$ – a gray substance, stable in air, insoluble in water and in 10% of NaOH and KOH solutions weakly interacts with concentrated solutions of HCl and H_2SO_4.

The structure of the $YbBi_4S_7$ compound belongs to the stibnite type (Sb_2S_3) with rhombic lattice periods: a = 11.27; b = 15.07; c = 7.88 Å, z = 5. The microhardness value is 1170 mPa, its pycnometric density and X-ray density (roentgenographic density) are 7.28 g/cm^3 and 7.65 g/cm^3, respectively. The $YbBi_2S_4$ – dark gray substance is stable in air, insoluble in water and alkalis. Mineral acids decompose it. $YbBi_2S_4$ and $YbSb_2S_4$ are isostructural and the first one crystallizes in the rhombic system with lattice parameters: a = 11.22; b = 14.75; c = 4.20 Å, z = 4.

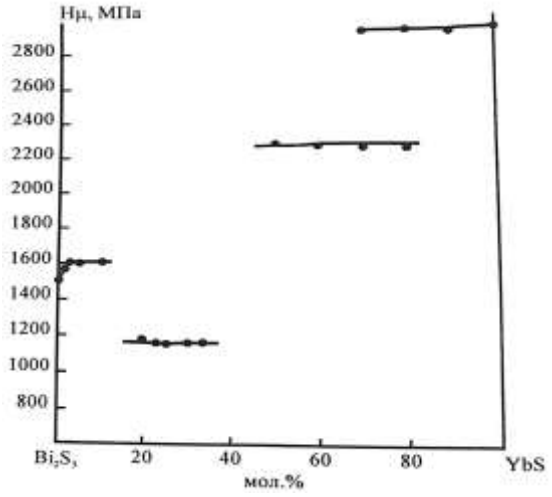

Fig. 2. The dependence of micro-hardness on the composition for the Bi_2S_3 – YbS system

The microhardness is 2280 MPa, and the pycnometric density of $YbBi_2S_4$ is 6.75 g/cm^3.

$YbBi_4S_7$ and $YbBi_2S_4$ compounds are p-type semiconductors (with holes).

Solid solutions obtained on the basis of bismuth sesqui-sulphide are crystallized in the rhombic system. The periods of the unit cell of the solid solutions increase with an increasing of the YbS content: a = 11.13 - 11.18; b = 11.27 ÷ 11.34; c = 3.97÷4.02 Å.

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Bi_2S_3 – YbS SİSTEMİ

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Fiziki-kimyəvi analiz metodları (DTA, RFA, MQA, mikrobərkliyin və sıxlığın təyini) ilə alınan nəticələrə əsaslanaraq Bi_2Se_3-YbS sistemində faza tarazlığı öyrənilmiş və onun hal diaqramı qurulmuşdur. Müəyyən edilmişdir ki, sistem kvazibinar olub, $YbBi_2S_4$ və $YbBi_4S_7$ tərkibli üçlü birləşmələrin əmələ gəlməsi ilə xarakterizə olunur. $YbBi_4S_7$ 1058 K-də konqurient, $YbBi_2S_4$ isə inkonqurient (1088 K) əriyir. Hər iki birləşmə ortorombik sinqoniyada kristallaşır.
Bi_2S_3-YbS sistemində Bi_2S_3 əsasında 8 mol% YbS tərkibli bərk məhlul sahəsi aşkar edilmişdir. YbS əsasında isə praktiki olaraq həllolma sahəsi müəyyən edilməmişdir.
Açar sözləri: *sistem, evtektika, konqruent, inkonqruent, hal diaqramı, Bi_2S_3, YbS.*

СИСТЕМА Bi_2S_3 – YbS

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Методами физико-химического анализа (ДТА, РФА, МСА, измерением микротвердости и плотности) изучено фазовое равновесие в системе Bi_2S_3 – YbS и построена диаграмма состояния. Установлено, что данная система является квазибинарным сечением тройной системы Yb-Bi-S. В системе выявлено образование двух тройных соединений состава $YbBi_2S_4$ и $YbBi_4S_7$. Определены области твердых растворов.
Ключевые слова: *система, эвтектика, конгруентное плавление, диаграмма состояния, Bi_2S_3, YbS.*