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PHASE RELATIONSHIP IN THE Bi-Bi_2S_3-BiI_3 TERNARY SUBSYSTEM

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Phase relationships in the Bi-S-I ternary system in the Bi-Bi_2S_3-BiI_3 have been investigated by means of DTA and XRD analyses. Existences of ternary compounds BiSI and $Bi_{19}S_{27}I_3$ has been confirmed, and the nature of their fusion specified. The phase diagram of polythermal section Bi-BiSI and the projection of the liquidus surface oh this subsyste have been built. Fields of primary crystallization of all components, types and coordinates of non- and monovariant equilibriums determined.

Keywords: *phase diagram, Bi-S-I ternary system, bismuth triiodide.*

1. INTRODUCTION

The study of phase diagram and thermodynamic properties of the Bi-S-I system is a part of systematic investigation of the A^V-X-I (A^V-As, Sb, Bi; X-S, Se, Te) [1–4]. These systems attract more attentions because many ternary phases in these systems are promising high-performance materials for ferroelectrics, piezoelectrics, thermoelectrics, photoconductors, piezoelastics [5–7] and recently discovered topological insulators or materials showing giant Rashba-type splitting [8]. With few exceptions many of these compounds either melt incongruently or decompose in the solid state, and therefore, their synthesis and, especially, crystal growth become a tricky problem [5]. The knowledge of the phase relationships and constructed phase diagrams can helps to solve these problems by the choice of initial compositions for growth of the large single-crystals of binary and ternary phases from melt.

Up to present, the phase diagram of the Bi-S-I ternary system has not yet been reported.

In the literature, there is only one report on the phase diagram of this system, devoted to the BiI_3-Bi_2Se_3 section [9]. According to this report, the section BiI_3-Bi_2Se_3 is quasi-binary and includes two ternary compounds BiSI and $Bi_{19}S_{27}I_3$ melting incongruently by the peritectic reactions at 808 K and 990K, respectively. The eutectic composition has the melting point of 668 K at about 4 mol % Bi_2S_3. The compositions of peritectic points lie at 35 and 80 mol % Bi_2S_3, respectively.

The crystal structures of both compounds are well studied. Haase-Wessel reported that [10] BiSI crystallizes monoclinically in the space group *Pnma* with a = 8.519(5) Å, b = 4.172(6) Å, c = 10.177(8) and z = 4. According to Ref. [11] $Bi_{19}S_{27}I_3$ has a hexagonal lattice, space group $P6_3^f$, with a = 15.640(2) Å, c = 4.029(2) Å and z = 2/3.

In this paper, we studied the phase relationships in the Bi-S-I ternary system in Bi-Bi_2S_3-BiI_3 concentration range in order to confirm the existence of ternary phases and phase relationships in this system, to provide useful information for searching new materials or preparing pure and high quality materials.

2. EXPERIMENTAL PART

2.1. Synthesis. Binary BiI, BiI_3 and ternary BiSI, $Bi_{19}S_{27}I_3$ were synthesized from the elements of a high purity grade (not less than 99.999%) in sealed (~10^{-2} Pa) silica ampoules following a specially designed method, which takes into account high volatility of iodine and sulfur. The synthesis was performed in an inclined two-zone furnace, with the hot zone kept at a temperature 20-30 K higher than the corresponding melting point of a synthesized

compound, whereas the temperature of the cold zone was about 400 K. After the main portion of iodine and sulfur had reacted, the ampoule was relocated in such a manner that the product could melt at 650 K (BiI), 700 K (BiI_3), 910 K (BiSI) and 1050 K ($Bi_{19}S_{27}I_3$). The melt was stirred at this temperature by shaking the furnace and then cooled with the furnace. Due to the peritectic character of formation of BiI, BiSI and $Bi_{19}S_{27}I_3$ they were subjected to a homogenizing annealing at 585, 750 and 950 K for 500 h. Bi_2S_3 was prepared by a one-step annealing of the stoichiometric mixture of the bismuth and sulfur at 1100 K, which is above the melting point of Bi_2S_3 (1048 K), followed by cooling with the furnace. We have prepared more than sixty alloys from the composition area Bi–BiI_3–S. As a rule, the all samples (total mass, 0.5 g) were obtained out of initial elemental components or preliminary synthesized compounds. After melting most of the alloys were annealed at 400 K and 360 K for 1000 h.

2.2. Analysis. X-ray powder diffraction (XRD) and differential thermal analysis (DTA) were used to analyze the samples. The XRD analysis was performed on a Bruker D8 ADVANCE diffractometer with Cu-Kα_1 radiation. For the DTA measurements, the NTR-72 device equipped with two chromel–alumel thermocouples was used. The ramp rate was 5 K m^{-1}. Temperatures of thermal effects were taken mainly from the heating curves. XRD confirmed that the pre-synthesized binary compounds were phase-pure.

3. RESULTS AND DISCUSSION

3.1. Isothermal sections of the Bi–S–I ternary system at 300 K

The isothermal sections of the Bi-Bi_2S_3-BiI_3 ternary system at 300 K (Fig. 1) confirm the formation of the both ternary compound BiSI and $Bi_{19}S_{27}I_3$. There are six three-phase regions in this subsystem. BiSI plays a key role in the distribution of the phase areas in subsolidus. This compound forms connod lines with another phases oh this subsystem.

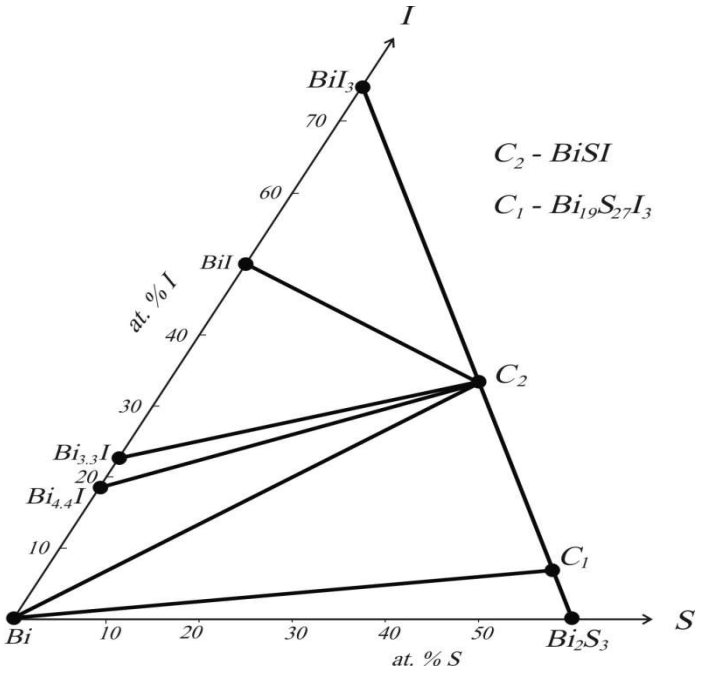

Figure 1. Isothermal section of the Bi-BiI_3-Bi_2S_3 system at 300K.

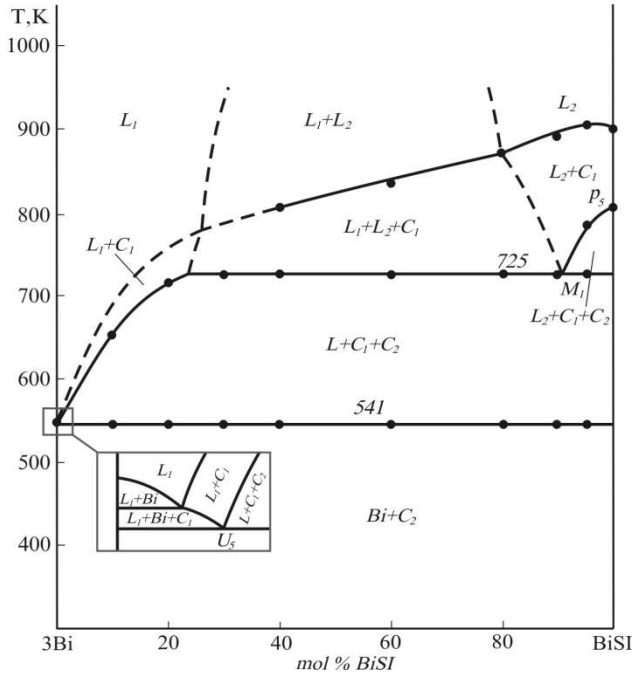

Figure 2. Polythermal section Bi–BiSI

3.2. The section Bi–BiSI (Fig. 2) characterized by a complicated reaction scheme. This section crosses the immiscibility area in the composition regions of 26-80 mol % Bi. In the solid state it is consist of two-phase mixture of BiI+C_2. This section clearly features two horizontal lines at 725 and 541 K, respectively, according to the invariant monotectic (M_1) and invariant transition (U_5) equilibriums. Below 725 K the both ternary compounds jointly crystallizes from liquid, while BiSI and Bi crystallizes by the invariant transition U_5 (Table 1) at 541 K. Schematic descriptions of some degenerate monovariant equilibriums and the phase areas very close to the elemental bismuth is given in Fig. 2 as blow-ups.

3.3. The liquidus surface of the Bi–S–I system

The liquidus surface of the Bi–S–I system in the Bi-Bi_2S_3-BiI_3 composition area consists of eight fields corresponding to the primary crystallization of the five binary, two ternary compounds and elemental bismuth (Fig.3). The fields of the primary crystallization of Bi_2S_3, BiSI and $Bi_{19}S_{27}I_3$ are very large and occupy more than 95% of the total area of this subsystem. Wide immiscibility field are observed in this system. It is starts from the Bi-I system (m_1m_1') and spreads into the Bi-BiI_3-Bi_2S_3 subsystem. Subsequently, the eutectic (e_3) and peritectic (p_5) curves from the BiI_3-Bi_2S_3 quasi-binary system pass through these fields and transform quadriphase monotectic equilibriums M_1 and M_2. The fields of the primary crystallization of the elemental bismuth and binary (BiI, Bi_7I_2 and Bi_9I_2) components as well as some invariant and monovariant equilibriums are degenerated very close to elemental bismuth. Schematic descriptions of these area are given in Fig. 3 as blow-ups. Table 1 summarizes the types and coordinates of nonvariant equilibriums, including the binary border subsystems, whereas Table 2 specifies the types and temperature intervals for the monovariant equilibriums.

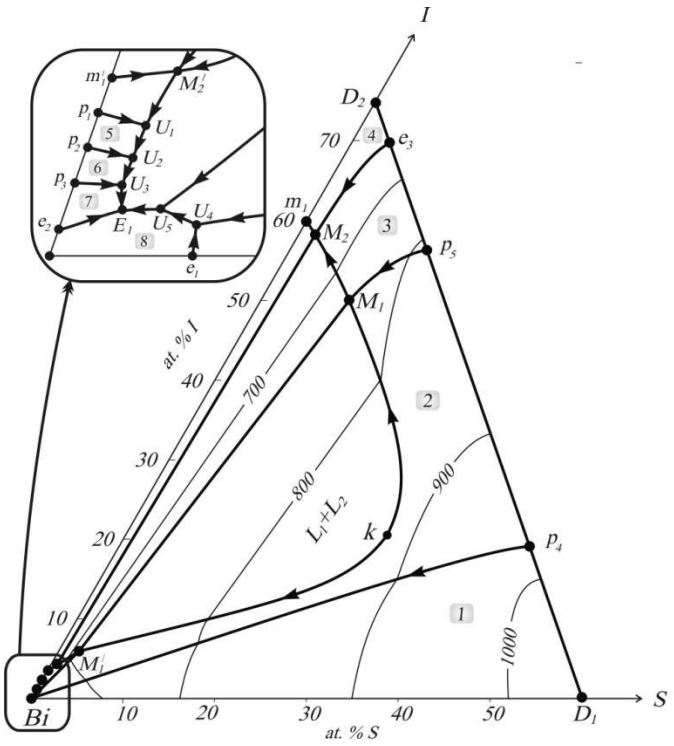

Figure 3. Projection of liquidus surface of the subsystem Bi-BiI_3-Bi_2S_3. Areas of primary crystallization of phases: 1 - Bi_2S_3; 2 - BiSI; 3 - $Bi_{19}S_{27}I_3$; 4 - BiI_3; 5 - BiI; 6 - Bi_7I_2; 7 - Bi_9I_2; 8 - Bi;

Table 1. Invariant equilibriums in the system Bi-Bi_2S_3-BiI_3

Point on Figure 6	Equilibrium	Composition, at.%		T,K
		S	I	
D_1	$L \Leftrightarrow Bi_2S_3$	60	-	1048
D_2	$L \Leftrightarrow BiI_3$	-	75	681
e_1	$L \Leftrightarrow Bi + Bi_2S_3$	>99	-	544
e_2	$L \Leftrightarrow Bi + Bi_9I_2$	>99	-	542
e_3	$L \Leftrightarrow BiSI + BiI_3$	3.5	70	668
p_1	$L + BiI_3 \Leftrightarrow BiI$	-	4	603
p_2	$L + BiI \Leftrightarrow Bi_7I_2$	-	2.5	573
p_3	$L + Bi_7I_2 \Leftrightarrow Bi_9I_2$	-	2	568
p_4	$L + Bi_2S_3 \Leftrightarrow Bi_{19}S_{27}I_3$	45	19	990
p_5	$L + Bi_{19}S_{27}I_3 \Leftrightarrow BiSI$	15	56.5	808
E_1	$L \Leftrightarrow Bi + Bi_9I_2 + BiSI$	-	-	540
U_1	$L + BiI_3 \Leftrightarrow BiI + BiSI$	-	-	600
U_2	$L + BiI \Leftrightarrow Bi_7I_2 + BiSI$	-	-	570
U_3	$L + Bi_7I_2 \Leftrightarrow Bi_9I_2 + BiSI$	-	-	565
U_4	$L + Bi_2S_3 \Leftrightarrow Bi + Bi_{19}S_{27}I_3$	-	-	542
U_5	$L + Bi_{19}S_{27}I_3 \Leftrightarrow Bi + BiSI$	-	-	541

$m_1(m_1^/)$	$L_2 \Leftrightarrow L_1 + BiI_3$	-	60	625
$M_1(M_1^/)$	$L_2 + Bi_{19}S_{27}I_3 \Leftrightarrow L_1 + BiSI$	11 (3)	50 (6)	725
$M_2(M_2^/)$	$L_1 + BiSI \Leftrightarrow L_2 + BiI_3$	2 (<1)	58 (4)	610

Notes: Conjugate invariant points and their compositions are in parentheses.

Table 2. Monovariant equilibriums in the system $Bi-Bi_2S_3-BiI_3$

Curves on Figure 6	**Equilibrium**	**Temperature ranges, K**
$e_5M_2\,(M_2^/U_1)$	$L_1(L_2) \Leftrightarrow BiSI + BiI_3$	668-600
e_5E_2	$L_2 \Leftrightarrow BiSI + BiI_3$	668-383
p_5M_1 ; p_5M_4	$L_1(L_2) \Leftrightarrow Bi_{19}S_{27}I_3 + BiSI$	808-541; 808-385
p_4U_4	$L + Bi_2S_3 \Leftrightarrow Bi_{19}S_{27}I_3$	990-542
$p_4M_3\,(M_3^/U_6)$	$L_1(L_2) \Leftrightarrow Bi_{19}S_{27}I_3 + Bi_2S_3$	990-386
p_1U_1	$L \Leftrightarrow BiI_3 + BiI$	603-600
U_1U_2	$L \Leftrightarrow BiI + BiSI$	600-570
p_2U_2	$L \Leftrightarrow Bi_7I_2 + BiI$	573-570
U_2U_3	$L \Leftrightarrow Bi_7I_2 + BiSI$	570-565
p_3U_3	$L \Leftrightarrow Bi_7I_2 + Bi_9I_2$	568-565
U_3E_1	$L \Leftrightarrow Bi_9I_2 + BiSI$	565-540
e_2E_1	$L \Leftrightarrow Bi_9I_2 + Bi$	542-540
e_1U_4	$L \Leftrightarrow Bi + Bi_2S_3$	544-542
U_4U_5	$L \Leftrightarrow Bi + Bi_{19}S_{27}I_3$	542-541
U_5E_1	$L \Leftrightarrow Bi + BiSI$	541-540

Notes: Conjugate monotectic curves are in parentheses.

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Bi-Bi_2S_3-BiI_3 SİSTEMİNDƏ FAZA TARAZLIQLARI

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Bi-S-I sistemində faza tarazlıqları Bi-Bi_2S_3-BiI_3 qatılıq sahəsində DTA və RFA üsulları ilə öyrənilmişdir. Bu qatılıq sahəsində BiSI və $Bi_{19}S_{27}I_3$ üçlü birləşmələrinin mövcudluğu təsdiq edilmiş, onların ərimə xarakteri dəqiqləşdirilmişdir. Bi-BiSI politermik kəsiyinin faza diaqramı və həmçinin, likvidus səthinin proyeksiyası qurulmuşdur. Sistemdə bütün komponentlərin ilkin kristallaşma sahələri, non- və monovariant tarazlıqların tipləri və koordinatları təyin edilmişdir.
Açar sözlər: *faza diaqramı, Bi-S-I sistemi.*

ФАЗОВЫЕ РАВНОВЕСИЯ В СИСТЕМЕ Bi-Bi_2S_3-BiI_3

З.С.Алиев, С.С.Мусаева, Ф.Я.Джафарли, О.А.Алиев, М.Б.Бабанлы

Методами ДТА и РФА изучены фазовые равновесия в системе Bi-S-I в области составов Bi-Bi_2S_3-BiI_3. Подтверждено существование тройных соединений BiSI и $Bi_{19}S_{27}I_3$, уточнен характер их плавления. Построены политермические разрезы фазовой диаграммы, а также проекция поверхности ликвидуса. Определены области первичной кристаллизации всех компонентов, типы и координаты нон- и моновариантных равновесий.
Ключевые слова: *фазовая диаграмма, система Bi-S-I.*

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