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THE A^V–B^{VI}–I TERNARY SYSTEMS: A BRIEF REVIEW ON THE PHASE EQUILIBRIA REVIEW

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Abstract. This paper presents a brief review on the ternary phase equilibria in the ternary A^V–B^{VI}–I systems (A^V = Sb, Bi; B^{VI} = S, Se, Te). These systems includes the series of ternary compounds those are very attractive source materials for photo-, thermos- and ferroelectric energy transformation along the recently discovered semiconductors that exhibit Rashba-type spin splitting in their surface states. In the Rashba semiconductors, a unique toroidal 3D Fermi surface appears on the crystal surface, which leads to unusual properties that make it possible to realize unique electronic devices based on these compounds. The thorough knowledge on the ternary phase diagram of these systems shed light on the chemical and structural design of new multifunctional materials with tunable properties. This knowledge is very important when focusing on the chemistry of such multifunctional materials based on complex element systems.

Keywords: phase diagram; phase equilibria; antimony sulfoiodide; bismuth selenoiodide; bismuth telluroiodide.

1. INTRODUCTION

Sulfo-, seleno- and tellurohalides of a group 15 metals have been intensively investigated over the last four decades as photo-, thermo- and ferroelectric materials [1–5]. During last four decades, there is an increasing interest for $A^VB^{VI}C^{VII}$-type ternary compounds due to their intriguing electronic properties, both in the single crystal form and thin film [6]. For example, SbSI was one of the most studied member of this family and so far, there is much information on its physical properties [7–12]. It has potential in applications ranging from optical light modulators, electroacousto-optical transformers, piezoelements to sensitive low-pressure gauges etc. On the other hand, since the giant Rashba-type spin splitting has recently been reported in the polar-layered non-centrosymmetric BiTeI [13–14], the bismuth containing tellurohalides became one of the much more attractive materials in the condensed matter physics [15–18]. These materials exhibit a strong spin-orbit interaction effect that opens a new pathway for the realization of spin-based electronic devices based on them.

Rational design and development of such ternary or quaternary new phases and solid solutions with a non-centrosymmetric crystal structure, as well as with a variable chemical composition, is of considerable interest for optimizing properties. Given the growing interest in this class of materials, a thorough study of phase diagrams for the respective element systems is of particular importance in the search for proper baseline compositions in order to develop materials with optimized properties [19–20]. Here, we focus on the reviewing of the ternary phase equilibria in the A^V–B^{VI}–I systems. This review can shed light on the chemical design of the new phases with variable compositions based on the starting multifunctional compounds of the systems, like SbSI, SbTeI, BiSI, BiSeI, BiTeI, etc.

2. PHASE DIAGRAMS OF THE A^V–B^{VI}–I SYSTEMS

2.1. The Sb-S-I system

As mentioned above, the Sb–S–I system has attracted much more attention thanks to its ternary compound SbSI which is most studied member of the family of $A^VB^{VI}C^{VII}$-type ternary compounds [1, 2, 7–12, 21]. Until our through investigation on this

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system, the binary SbI_3–Sb_2S_3 section was only studied in this system. Two different literature reports exist on the phase diagram of this section [22, 23]. Belyayev [22] reported that this section includes the only compound SbSI, which melts congruently at 650 K. The eutectic composition between SbSI and Sb_2S_3 has the melting point of 595 K at about 75 mol % Sb_2S_3, whereas the eutectic between SbSI and Sb_2S_3 is degenerated close to SbI_3 at 443 K. Ryazantsev and co-authors [23] reported slightly different data on the melting point of SbSI and eutectic compositions. SbSI melts congruently at 675 K according to this work and has a narrow homogeneity region. Our DTA, XRD data and the results of the microhardness for the selected compositions [24] (Fig. 1) agree well with the data of Ref. [23]. The congruent melting temperature of SbSI was determined to be 675 K which agrees well with reported data [23] whereas 25 °C higher than data of [22]. The main discrepancy is related to the form of the liquidus curve of SbSI. According to our data, the liquidus surface of SbSI has a *S*-shape form, which is typical for the systems that have a tendency for immiscibility, however, it represented as convex curve in Ref. [23] typical for dystectic type equilibrium. The crystal structure of SbSI is reported in the literature [25, 26]. Three phases of this compound have been reported: ferroelectric (T < 295 K), antiferroelectric (295 K<T<410 K) and paraelectric (T < 410 K) [1]. Both in the paraelectric and ferroelectric phase, it crystallizes in the orthorhombic structure with space group *Pnam* (a = 8.556(3) Å; b = 10.186(4) Å; c = 4.111(2) Å; z = 4) and $Pna2_1$ (a = 8.53 Å; b = 10.14 Å; c = 4.10 Å), according to [25] and [26], respectively. As can be seen from the global phase diagram of the system, (Fig. 2) [24], the primary crystallization field of the SbSI is quite large and occupies considerable part of the total area of the composition triangle, which provides a variety of compositions of the melts for growing single crystals of the SbSI. However, the largest primary crystallization field belongs to elemental antimony. Two wide immiscibility fields were detected in this system. The first one (L_1 + L_2) starts from the Sb–I system (m_3m_3') and joins to immiscibility field of the Sb-Sb_2S_3 subsystem (m_1m_1') over the Sb–SbSI section (m_4m_4'). It almost covers the primary crystallization field of antimony in the Sb–SbI_3–Sb_2S_3 subsystem. The primary crystallization field of elemental sulfur and some in- and monovariant equilibria are degenerated and is positioned very close to the elemental sulfur corner of the composition triangle. A schematic description of this area is given in Fig. 2 as a blow-up inset.

2.2. The Sb-Se-I system

The literature review shows that the ternary Sb–Se–I system was investigated so far along the various isopleth sections. However, among them the quasi-binary Sb_2Se_3–SbI_3 section was the most studied one [27, 28–32]. According to Ref. [28] this section hosts the only compound SbSeI that melts congruently at 721 K, whereas the eutectic compositions were found to be 69 and 3 mol % Sb_2S_3 at temperatures 703 and 428 K, respectively. Other authors [29, 30] report slightly different data on the melting points and eutectic compositions. The thermal analysis results in our previous investigation [27] for the selected alloys in this system showed the well coincidence with the data reported by Dolgikh and co-authors [29]. The congruent melting character of the SbSeI at 725 K is confirmed. Its eutectic mixture with the Sb_2Se_3 crystallizes at 58 mol % Sb_2Se_3 at 716 K whereas, the eutectic with SbI_3 is almost degenerated (Fig. 3) [27]. The SbI_3–Se and SbSeI–Se quasi-binary sections are shown to be of eutectic type. The eutectic compositions have melting point of 433 and 428, respectively, and have 62 and 74 mol % Se [31]. SbSeI crystallizes in the SbSI structure type, space group *Pnma*, with the unit cell parameters a = 8.6862(9), b = 10.3927(9), c = 4.1452(3) Å [4]. The self-consistent phase diagram of the Sb–Se–I system [27] (Fig. 4) was plotted by us at first time. It consists of six fields corresponding to primary crystallization of the elemental components

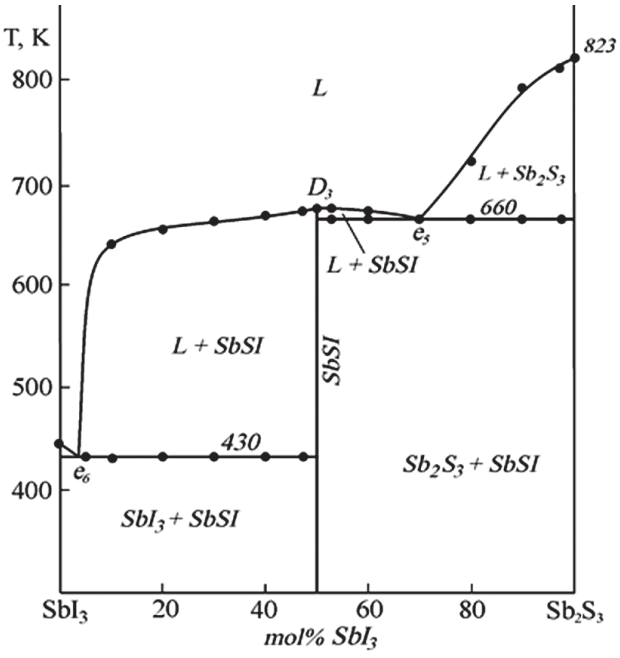

Fig. 1. Phase diagram of the SbI_3–Sb_2S_3 quasi-binary system [23, 24]

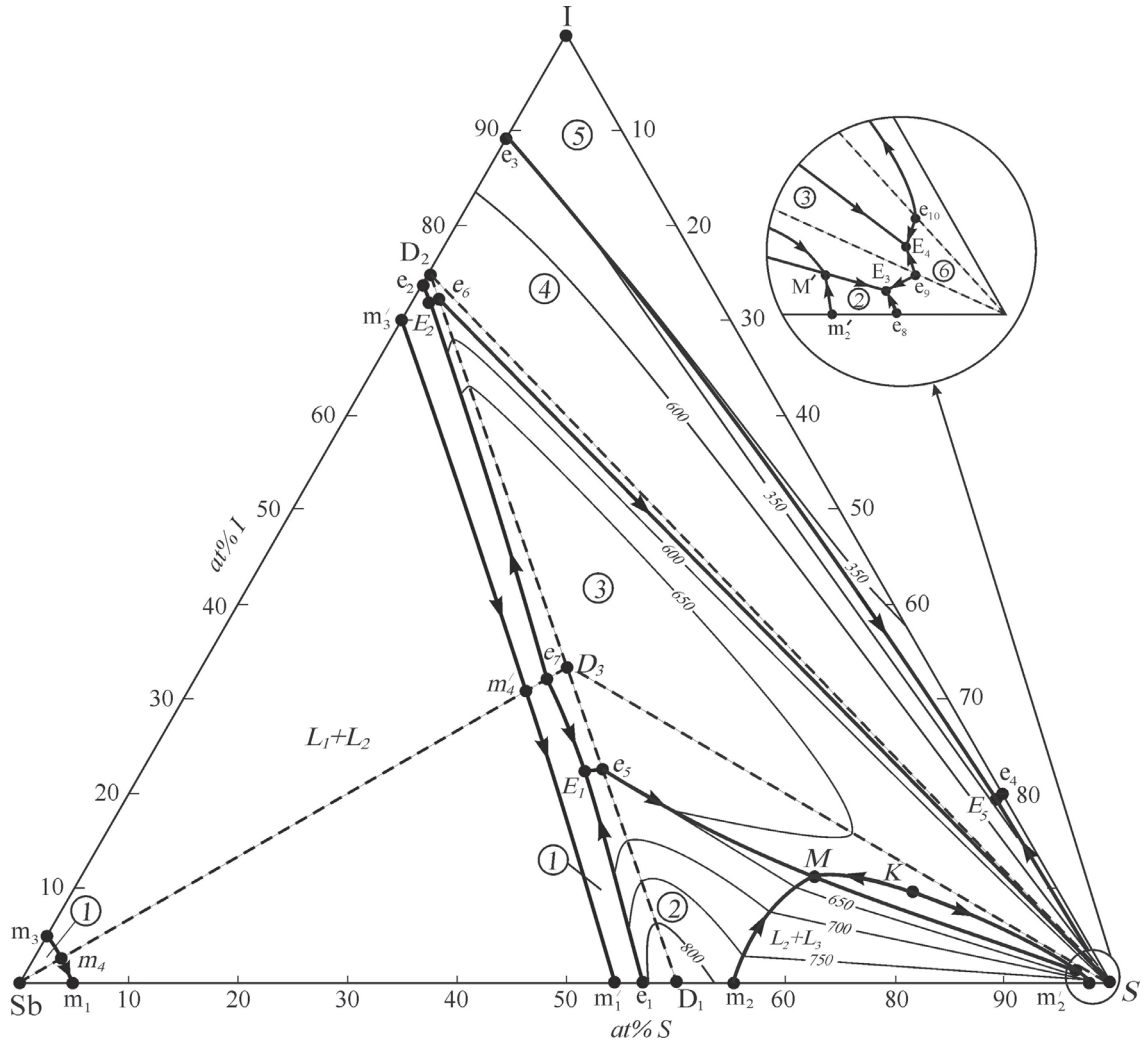

Fig. 2. The phase diagram of the Sb–S–I system [24]. Primary crystallization fields of the phases: 1 – Sb; 2 – Sb_2S_3; 3 – SbSI; 4 – SbI_3; 5 – I_2; 6 – S

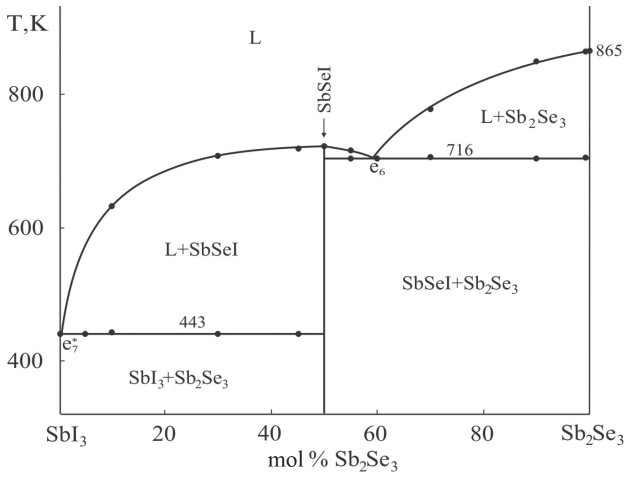

Fig. 3. Phase diagram of the SbI_3–Sb_2Se_3 system [29]. Black dots show our data [27]

and compounds Sb_2Se_3, SbI_3 and SbSeI. Similar to Sb–S–I system, it also exhibits the broad immiscibility region ($m_1m_3m_2m'_2m'_3m'_1$), which lies within the field of primary crystallization of antimony and overlaps with 90 % of its area. The quasi-binary sections (dashed lines in Fig. 4) triangulate the Sb–Se–I system forming five independent subsystems. They are Sb–Sb_2Se_3–SbSeI, Sb–SbI_3–SbSeI, SbSeI–SbI_3–Se, Sb_2Se_3–SbSeI–Se, and SbI_3–Se–I_2. The two former subsystems are characterized by monotectic and eutectic equilibria whereas; the other subsystems belong to the ternary eutectic type.

2.3. The Sb–Te–I system

The literature data on the phase equilibria of Sb–Te–I system contained several reports on various isopleth sections [32, 33–37], among which the quasibinary Sb_2Te_3–SbI_3 section was the most stu-

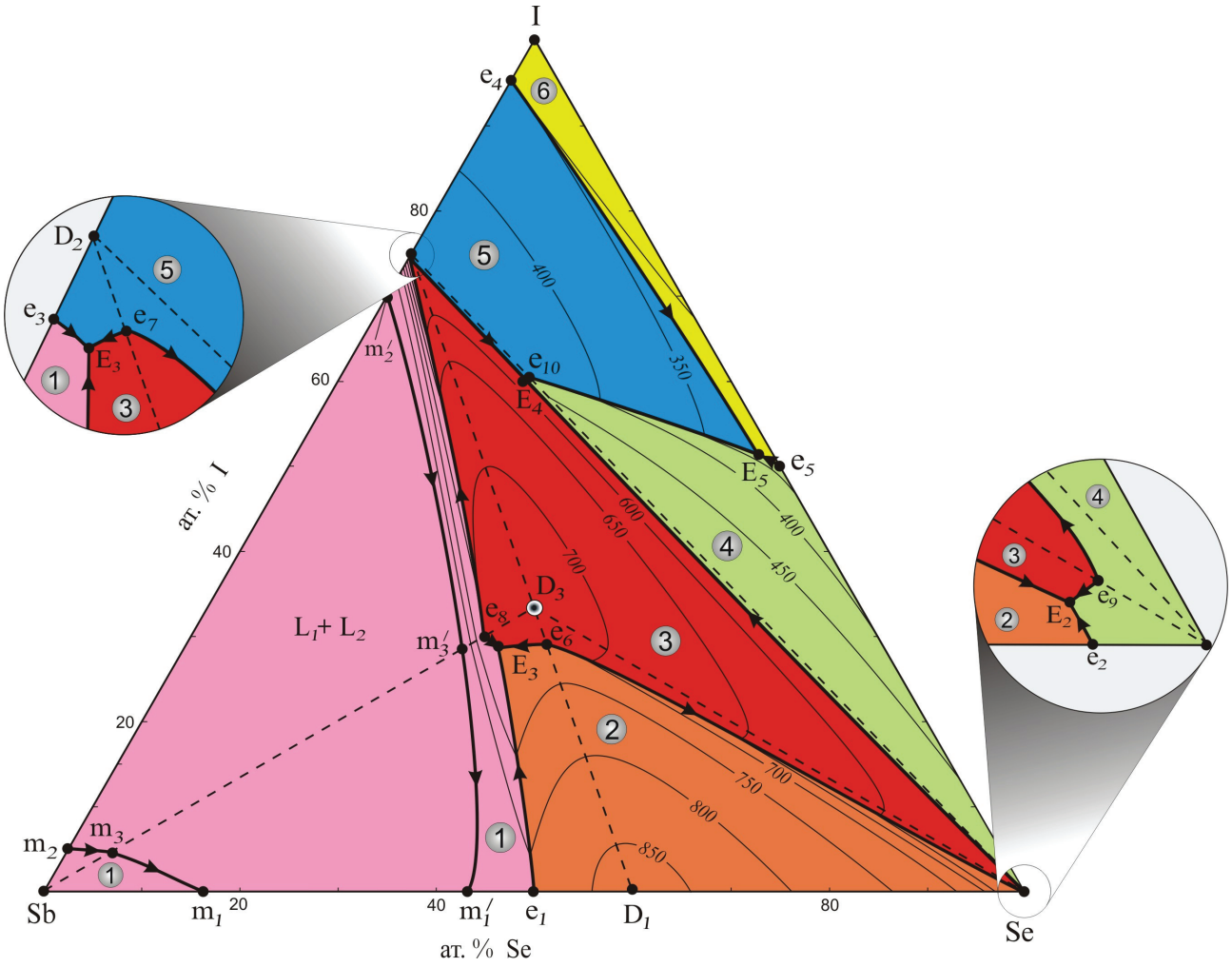

Fig. 4. The phase diagram of the Sb–Se–I system [27]. Primary crystallization fields are: 1 – Sb; 2 – Sb_2Se_3; 3 – SbSeI; 4 – Se; 5 – SbI_3; 6 – I_2

died [8 –12]. Belotskiy shown [33, 34] that the section Sb_2Te_3–SbI_3 contains the only compound SbTeI, which melts congruently at 633 K. Other authors [35-37] report results that are different from those of Belotskiy's data [33, 34]. These works show that the ternary compound SbTeI melts incongruently by a peritectic reaction at 643 [35, 36] or 675 K [37]. Our DTA data and the results of the microhardness and EMF measurements for the selected compositions confirm the data of [35, 36], (Fig. 5).

SbTeI is the only ternary compound in the Sb–Te–I system. It crystallizes in the monoclinic space group *C2/m* with the unit cell parameters $a = 13.701$, $b = 4.2418$, $c = 9.201$ Å [38]. Its crystal structure represents a unique monoclinic variation of the SbSI structure type [39], in which typical for these structures (SbTe) double chains run along the *b* axis and alternate with the iodine atoms in the ac plane. Such a monoclinic distortion of the SbSI type is stable and persists even when 90 % of the antimony is re-

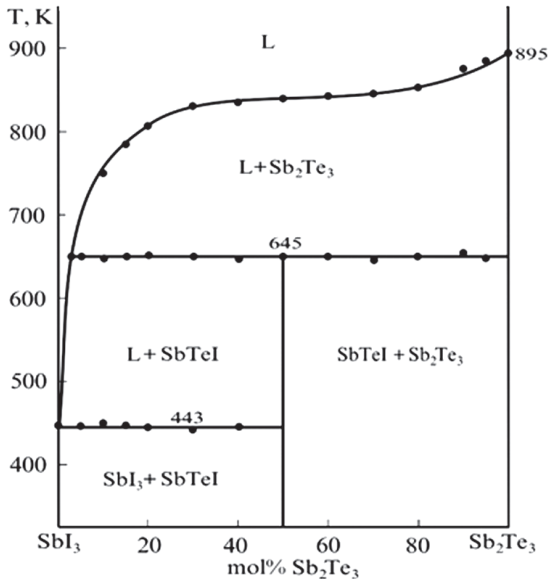

Fig. 5. Phase diagram of the SbI_3–Sb_2Te_3 system [35, 36]. Black dots shows our data [32]

placed by bismuth and transforms into the trigonal BiTeI structure only with greater bismuth concentration [40, 41]. The complete phase diagram of the ternary Sb–Te–I system has been investigated by us in [32]. The system (Fig. 6) have a quite complex phase relationships [32]. One can see that the area of the primary crystallization of SbTeI is degenerate near SbI_3 indicate that grows of its large single crystal from melt is a difficult process. The system Sb–Te–I is divided by three quasi-binary sections in the following four independent subsystems: SbI_3–TeI_4–I_2 (A), SbI_3–TeI_4–Te (B), SbI_3–Te–Sb_2Te_3 (C) and Sb–SbI_3–Sb_2Te_3 (D). The subsystem (A) relates to the invariant eutectic type, whereas the wide immiscibility region was found in the subsystem (B). The subsystem (C) is characterized by eutectic and monotectic reactions, whereas the existence of the eutectic, monotectic and transition reactions and a wide immiscibility region characterize the subsystem (D).

2.4. The Bi–S–I system

The complete phase diagram of the Bi–S–I ternary system has been reported in our paper [42] at first itme. Nevertheless, up to this report only the quais-binary BiI_3–Bi_2S_3 system was studied by Ryazantsev et al. [43]. According to this work, it is a quasi-binary one and includes two ternary compounds, namely BiSI and $Bi_{19}S_{27}I_3$. These compounds melt peritectically at 808 and 990 K, respectively. The compositions of the peritectic points along the section lie at 35 and 80 mol % Bi_2S_3, respectively. The eutectic reaction was found to occur at 668 K and 4 mol % Bi_2S_3. The thermodynamic properties of the both ternary compounds in this system were obtained by Oppermann and Petasch [44]. Our DTA and XRD results for the selected compositions agree well with the result of [43] (Fig. 7). The detailed investigations confirm the existence both of ternary compounds BiSI and $Bi_{19}S_{27}I_3$. The crystal structures of both compounds are well studied. BiSI crystallizes in the orthorhombic space group *Pnma* with the lattice parameters $a = 8.529$, $b = 4.172$, $c = 10.177$ Å and $z = 4$ [45]. $Bi_{19}S_{27}I_3$ has a hexagonal lattice, space group $P63/m$, with $a = 15.640$, $c = 4.029(2)$ Å, and $z = 2/3$. BiSI crystallizes in the BiSCl structure type (also referred to as the SbSBr type) and features one-dimensional BiSI strands with the considerably elongated Bi–I distance of 3.0 Å that run along

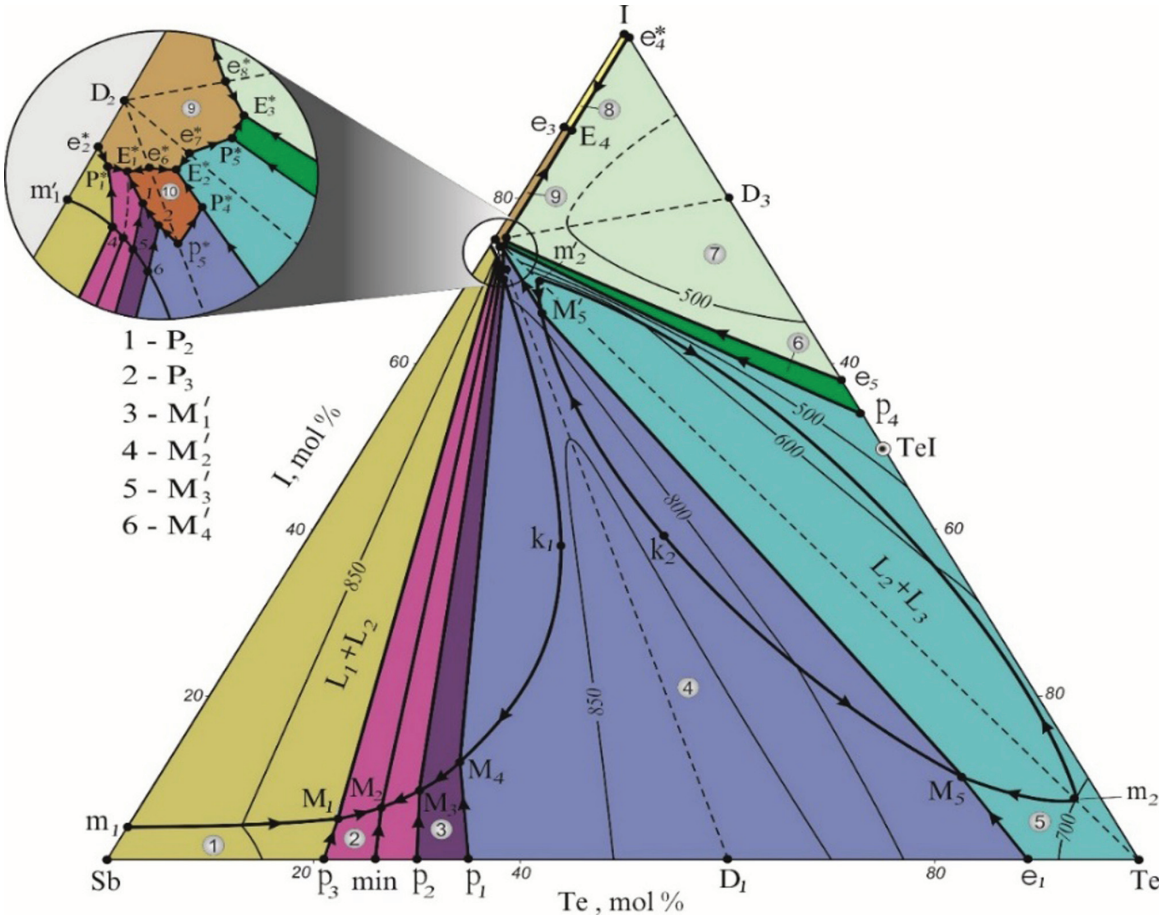

Fig. 6. The phase diagram of the Sb–Te–I system [32]. Primary crystallization areas of phases: 1 – α; 2 – δ; 3 – γ; 4 – Sb_2Te_3; 5 – Te; 6 – TeI; 7 – TeI_4; 8 – I_2; 9 – SbI_3; 10 – SbTeI

the c axis. The slabs are joined into a 3D structure through non-covalent Bi–I interactions at 3.7 Å. In the crystal structure of $Bi_{19}S_{27}I_3$, the slabs running along the c axis are formed only by bismuth and sulfur atoms; they are further connected through disordered Bi(1) atoms, whereas the iodine atoms sit in the voids, with the Bi–I distances exceeding 3.5 Å. Taking into account the details of the crystal structure of $Bi_{19}S_{27}I_3$, it is frequently formulated as $Bi(Bi_2S_3)_9I_3$ [45]. The phase diagram of the system (Fig. 8) [42] shows the existence of the ten primary crystallization fields. The primary crystallization fields of the binary BiI_3 Bi_2S_3 and ternary $Bi_{19}S_{27}I_3$, BiSI compounds are found to be very large and occupy major part of the total area of the Bi–S–I triangle. Two wide immiscibility fields are observed in this system. The first one ($L_1 + L_2$) starts from the Bi–I system (m_2m_2') and spreads into the Bi–BiI_3–Bi_2S_3

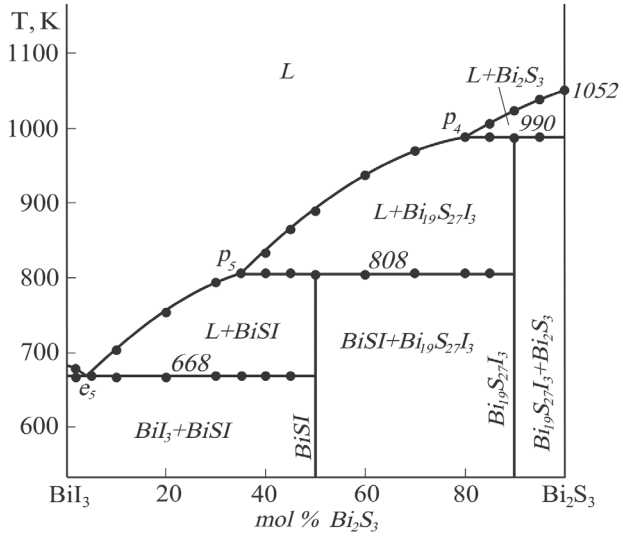

Fig. 7. Phase diagram of the BiI_3–Bi_2S_3 system [43, 44]

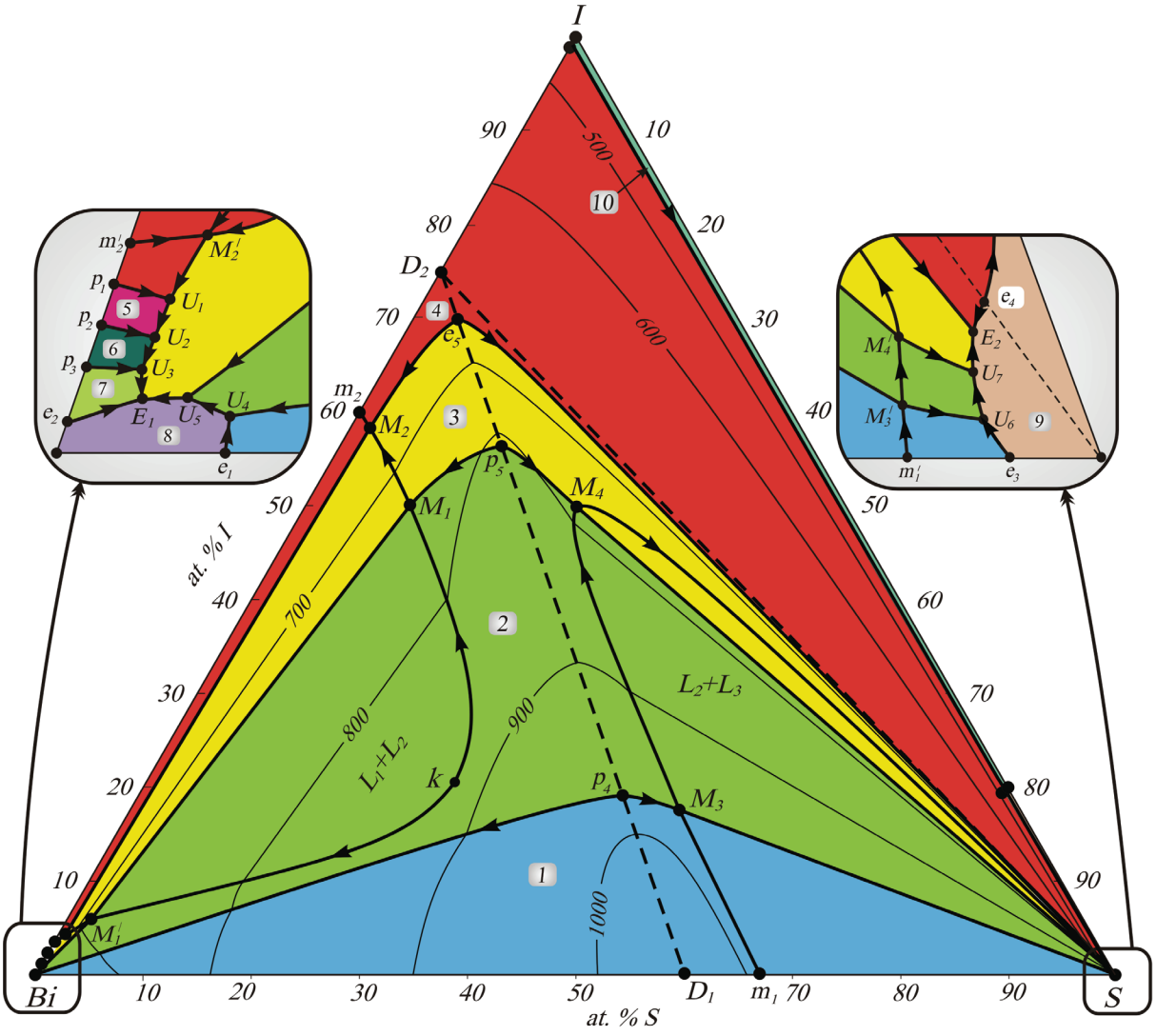

Fig. 8. The phase diagram of the Bi–S–I system [42]. Primary crystallization fields: 1 - Bi_2S_3; 2 - BiSI; 3 - $Bi_{19}S_{27}I_3$; 4 - BiI_3; 5 - BiI; 6 - Bi_7I_2; 7 - Bi_9I_2; 8 - Bi; 9 - S; 10 - I_2

subsystem whereas the second one (L_2+L_3) starts from the Bi_2S_3–S subsystem (m_1m_1') and spreads into the Bi_2S_3–BiI_3–S subsystem.

2.5. The Bi–Se–I system

Similar to analogous ternary systems this system also investigated mostly along the Bi_2Se_3–BiI_3 section. Different groups of researchers have studied this system and reported either inapropriate or contradictory results. Turjanica [47] and Belotskii [48] decided that these system hosts two ternary compounds, namely BiSeI and $Bi_{19}Se_{27}I_3$, while Dolgikh [49, 50] refutes the existence of the latter one. According to phase diagram drawn by Turjanica [47] and Belotskii [48] the BiSeI melts congruently at 808 K whereas, the latter one forms by peritectic reaction occur at 943 K. However, Dolgikh [49, 50] shows that the only compound, BiSeI is exist in the system and it melts incongruently at 805 K. The latest version of the Bi_2Se_3–BiI_3 phase diagram is given in the [51] (Fig. 9). One can see that, the melting temperatures for the BiSeI compound determined in [47], [49] and [51] are very close, however, they are differ just for type of formation reaction. The phase diagram represented in [51] is very rare case that shows transition from a dystectic type to a peritectic one. This type phase diagram is possible in principle and here, there is no violation of the Gibbs phase rule. However, only thorough investigations in this area can show the correct type of formation reaction of BiSeI.

The crystal structure of the BiSI studied by various authors [52, 53]. It crystallizes in the SbSI type orthorhombic lattice system with the space group *Pnma* and lattice parameters a = 8.697(2), b = 4.221(1), c = 10.574(2) Å and z = 4 [53]. The phase equilibria along the BiSeI–Bi and BiSeI–BiI systems were studied by Chervenyuk et al. [54]. It was found that the former one belongs to simple eutectic type, while the latter one featured by eutectic and monotectic phase diagram.

2.6. The Bi–Te–I system

The phase diagram of the Bi–Te– I system for the entire concentration range was first investigated by us [55]. The series of isopleth sections and the liquidus surface projection were constructed. The fields of the primary crystallization, as well as the types and coordinates of non- and monovariant equilibriums were determined. Prior to our experimental work on this ternary system, it was studied in a series of works [56–58]. The greatest number of results [57–58] is devoted to the study of phase equilibria in the quasi-binary system Bi_2Te_3–BiI_3. The results of [57–58] are very similar and show that the phase diagram of this system relates to a dystectic type with ternary compound BiTeI with a melting temperature of 828±5K (Fig. 10). Belotskiy [33, 34] determined the melting temperature of BiTeI as 743 K and some fragments of the Bi_2Te_3–BiI_3 phase diagram are a little bit different than those of reported in Refs. [56–58]. BiTeI crystallizes in hexagonal structure of type CdI_2 with space group *P*-3*ml*, the lattice parameters: a = 4.31 Å, c = 6.83 Å, z=1, [56] and a = 4.3392 Å, c = 6.854 Å, z=1 [41]. Other isopleth sections BiI_3–Te and BiTeI–Te are studied by Evdokimenko [59] and reported as simple eutectic type. Savilov [60] reported at first the exis-

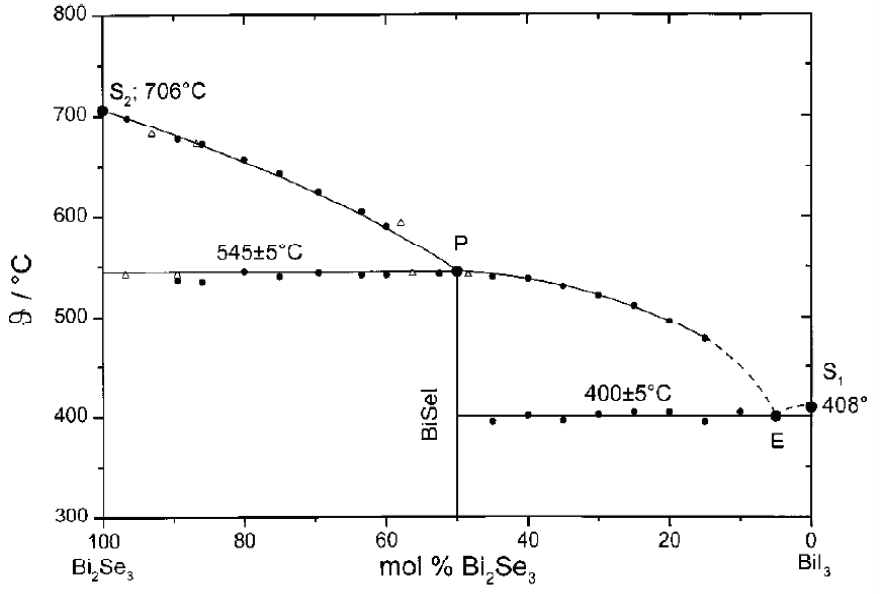

Fig. 9. Phase diagram of the quasi-binary BiI_3–Bi_2Se_3 system [51]

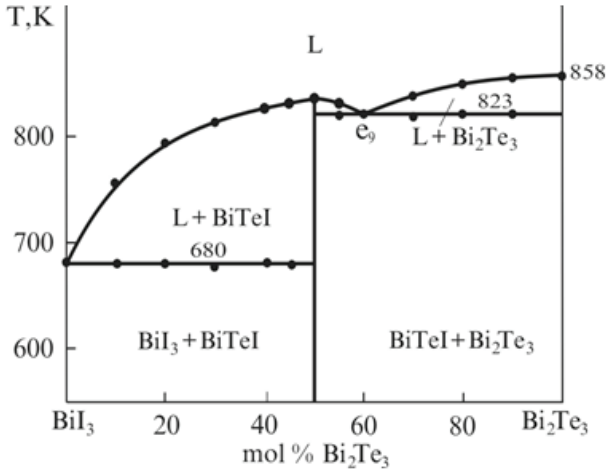

Fig. 10. Phase diagram of the BiI_3–Bi_2Te_3 system [56-57]. Black dots shows our data [55]

tence of two new lowest telluroiodides of bismuth Bi_2TeI and $Bi_4TeI_{1.25}$(or $Bi_{16}Te_4I_5$) obtained by condensation from the gas phase. Single crystals of the former one obtained from a melt. This compound have a monoclinic type crystal structure with lattice parameters: a = 7.586 Å, b = 4.380 Å, c=17.74 Å. The global phase diagram was constructed by us [55], where those ternary compounds were verified, their melting characters and temperatures determined. Standard thermodynamic functions of formation were also determined. The phase diagram (Fig. 11) shows the feasibility to prepare bulk single crystals of ternary compounds BiTeI, Bi_2TeI, and $Bi_4TeI_{1.25}$ by directional crystallization of solution melts. The quasi-binary sections divide the system Bi–Te–I on five independent subsystems: BiI3–TeI_4–I, BiI_3–TeI_4–Te, BiI_3–BiTeI–Te, Bi_2Te_3–BiTeI–Te and Bi–Bi_2Te_3–BiI_3.

3. CONCLUSIONS

A comparative analysis of the literature data that known so far, allows to establish that the chalcoiodide systems of the antimony and bismuth exhibit very complex phase equilibrium scheme in the whole systems. They are characterized by immiscibility areas that comes from boundary binary systems. This brief review on phase diagram of these

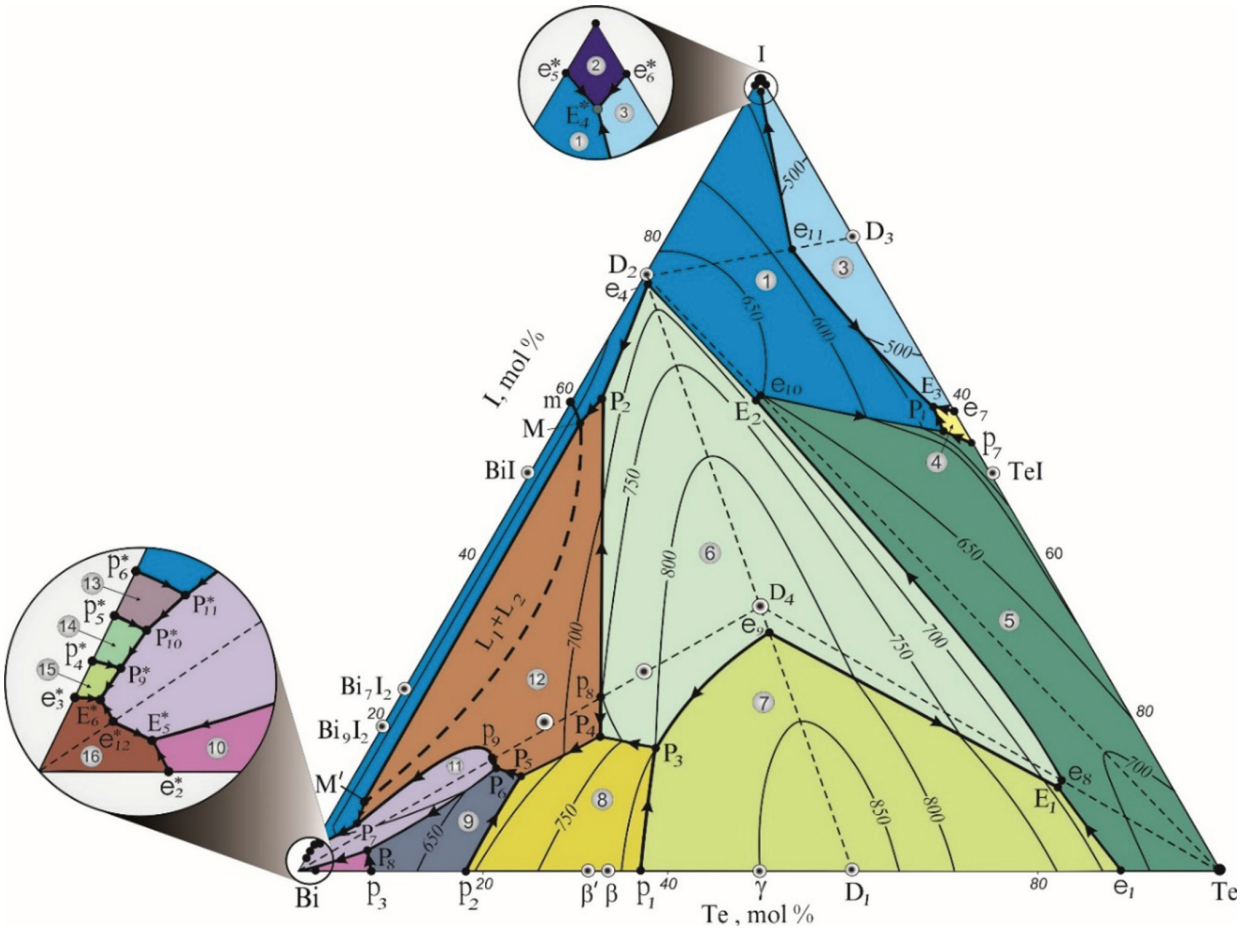

Fig. 11. The liquidus surface projection of the Bi–Te–I system [55]. Primary crystallization fields: 1 – BiI_3; 2 – I_2; 3 – TeI_4; 4 – TeI; 5 – Te; 6 – BiTeI; 7 – Bi_2Te_3; 8 – γ; 9 – β; 10 – β′; 11 – $Bi_4TeI_{1.25}$; 12 – Bi_2TeI; 13 – BiI; 14 – Bi_7I_2; 15 – Bi_9I_2; 16 – Bi

systems provides very valuable information for optimizing the synthesis and growth conditions of their known starting and intermediate ternary phases. Particularly, the considered systems are of significant importance in terms of the rational design of new multifunctional phases with variable and non-variable chemical compositions. On the other hands, information on the ternary phase diagrams of the mentioned systems are very important in growth of large single crystals from both stoichiometric and non-stoichiometric liquid phases.

CONFLICT OF INTEREST

The author declares the absence of obvious and potential conflicts of interest related to the publication of this article.

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ТРОЙНЫЕ СИСТЕМЫ A^V–B^{VI}–I: КРАТКИЙ ОБЗОР ФАЗОВЫХ РАВНОВЕСИЙ ОБЗОР

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Аннотация. В работе представлен краткий обзор по фазовым равновесиям в тройных системах A^V–B^{VI}–I (A^V = Sb, Bi; B^{VI} = S, Se, Te). Эти системы характеризуются образованием ряда тройных соединений, являющихся перспективными базовыми материалами для фото-, термо- и ферроэлектрических преобразователей энергии. Некоторые из них демонстрируют гигантское спиновое расщепление Рашба, в результате чего на поверхности кристалла возникает уникальная тороидальная 3Д поверхность Ферми, которая приводит к необычным свойствам, открывающим возможность реализации на основе этих соединений уникальных электронных устройств. Разработка методов направленного синтеза указанных соединений и мультифункциональных материалов

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на их основе базируется на данных по фазовым равновесиям в соответствующих системах.

Ключевые слова: фазовая диаграмма; фазовые равновесия; сульфоиодид сурьмы; селеноидид висмута; теллуройодид висмута.

КОНФЛИКТ ИНТЕРЕСОВ

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