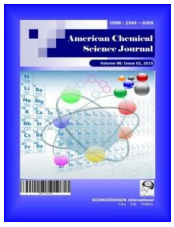

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Chemistry of Thallium-based Topological Insulators

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Authors' contributions

This work was carried out in collaboration between all authors. Author MBB managed the literature searches and wrote the manuscript. Authors YIJ and ZSA systematized the literature data on phase equilibria. Author IRA analyzed the crystallographic data and wrote part 5. All authors read and approved the final manuscript.

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Review Article

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ABSTRACT

The goal of this review is to briefly introduce the chemistry of the topological insulators (TIs) based on thallium chalcogenides. Numerous phase diagrams of ternary Tl-B^V-X (B^V – Sb, Bi; X – Se, Te) systems having TlB^VX_2 type compounds which exhibit spin polarized topological surface state is evaluated and compiled. Published data on the phase equilibria in the quaternary Tl-Sb-Bi-X and Tl-BV-X-X′ systems are also reviewed and it has been revealed that their quasiternary Tl_2X-Sb_2X_3-Bi_2X_3 and reciprocal $3Tl_2X+B^V_2X'_3 \leftrightarrow 3Tl_2X'+B^V_2X_3$ subsystems form a wide range of solid solutions based on compounds TlB^VX_2 and $B^V_2X_3$, whose both confirmed as potential 3D TIs materials. All phase diagrams of respective systems offer profound possibilities for growth their large single crystals from melt.

Keywords: Thallium-bismuth (antimony) chalcogenides; topological insulators; phase diagrams; solid solutions; crystal growth.

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1. INTRODUCTION

In last few years, tetradymite-like binary and ternary layered chalcogenides of bismuth and antimony are as well as some Tl-based materials attracting renewed interest because they are represents a new phase of quantum matter with innovative electronic properties. These materials, called "Topological Insulators" (TIs), are insulators in the bulk, but they have surface states which imply metallic conduction at the surface due to the existence of well-defined topological surface states (TSS). The charge carriers of these states are spin-polarized and fully protected by the time-reversal symmetry (TRS) from the backscattering by defects, which results in nearly dissipationless current. Allowing electrons to move along their surface, but not through their inside, they emerged as an intriguing material platform for the exploration of exotic physical phenomena, somehow resembling the graphene Dirac cone physics, as well as for exciting application capabilities mainly in spintronics, quantum computing, low-power electronics and optoelectronics [1-5].

In 2004, Charles Kane co-authors [6.7] have predicted possibility of materials that can demonstrate the quantum spin Hall effect without external magnetic fields and ultralow temperatures. According to their calculations such materials due to the magnetic field of their nuclei of atoms may generate spin-coordinated behavior of electrons even at room temperature. This innovative work has stimulated new theoretical researches. Soon, the Joel Moore et al [8,9] showed that the three-dimensional crystals can also demonstrate similar quantum effects on the surface, being insulators in the bulk. They called these hypothetical materials "topological insulators".

In 2008, it was discovered that $Bi_{1-x}Sb_x$ solid solutions well defined TSS in the semiconductor field [10]. Later, the same electronic state have been unveiled in compounds Bi_2Se_3, Bi_2Te_3, Sb_2Te_3 [11,12]. Since, huge attention has been afforded not only by physicists, but also chemists and materials scientists around the world to study of this new unique class of functional materials. Nowadays, in addition to the above pointed binary compounds [13-19] TIs properties also found in ternary tetradymite-like compounds of A^{IV}-B^{V}-Te systems [16,20-24] as well as some bismuth tellurohalides [25-30]. Recent studies have shown that the compounds of $TlB^{V}X_2$ type also exhibit the TIs properties [31-34].

The development of magnetizm inTIs is also "hot topic" in few recent years [35-40]. Stated above binary and ternary compounds also serve as a good matrix for design of new materials with desired properties. The realization of many of the predicted topological phenomena requires tuning of the topological surface state of TIs and this is can be achieved by doping or intercalation. In particular, doping with magnetic impurities can open new perspectives for spintronics and spin caloritronics applications. It has been recently predicted and demonstrated that they can become ferromagnetic upon doping. In combination with ferromagnets TIs can be used also for a creation of a new type of spin torque devices for magnetic memory applications. Hence, development of ferromagnetism in TIs is a key factor to realize the spin related new applications and magnetic doped TIs are intriguing candidates for future low-power electronic and spintronic devices.

In this review, the data on phase diagrams of the ternary Tl-B^{V}-X (B^{V}-Sb,Bi; X-Se,Te) and quaternary Tl-Sb-Bi-X, Tl-B^{V}-X-$X^{/}$ systems are systematically evaluated.

2. THE ROLE OF PHASE DIAGRAMS IN THE DESIGN OF TIs

The development of new multicomponent materials, including TIs, first of all required studying the phase equilibria in the relevant systems and the plotting the phase diagrams. The phase diagrams allow identifying new chemical compounds or phases of variable composition, as well as establishing their formation character, primary crystallization and homogeneity areas, phase transformations, etc. All these displayed data plays an important role in development or modification of methods for synthesis and crystal growth [41].

Almost all of the binary and ternary compounds with the TIs properties, and solid solutions based on them are thermodynamically stable and have been published in their equilibrium phase diagrams and thermodynamic properties were investigated in numerous studies and are routinely used for their synthesis with a given composition, growth of single crystals [42-44].

As it has been known, the melting temperature (primary crystallization) of the almost all member of the Bi_2Se_3 family TIs does not exceed 1000 K which the vapor pressure of more volatile components of these compounds: tellurium (T_b =

1263 K) and selenium (T_b = 958 K) is quite low [45]. The starting elementary components of those compounds and they themselves do not react with quartz up to this temperature limit. Therefore, these compounds are usually synthesized by melting elemental components in a quartz ampoule under a vacuum or inert atmosphere.

The information in the phase diagrams is especially valuable for the development or modification of techniques for direct synthesis of samples and their crystals growing from melts and solutions by directed crystallization.

The vertical Bridgman-Stockbarger and Czochralski methods as well as horizontal direct crystallization for the growth of large single crystals of TIs compounds the crystallization from the melt are routinely used techniques [46]. The detailed description of the above methods and their different modifications can be found elsewhere [47-49].

3. PHASE DIAGRAMS OF THE TERNARY Tl-B^V-X (B^V-Sb, Bi; X-Se, Te) SYSTEMS

In ternary Tl-B^V-X systems thermodynamically stable phases formed on certain quasibinary section. Therefore, for the preparation of single crystals of many ternary compounds, the *T-x* diagrams of the corresponding quasi-binary systems are often used. More comprehensive information on the character of phase equilibria in the ternary systems are representing as a projection of the concentration triangle. Similar diagrams allow varying the solution-melt composition along the primary crystallization surface of grown phase and its crystallization temperature in a broader range.

Phase equilibria in the Tl-B^V-X systems have been reported in numerous research works [50-69].

3.1 The Tl-Sb-Se System

The quasibinary section Tl_2Se-Sb_2Se_3 of this system studied in [50-55]. According to Ref. [50], three ternary compounds, namely $TlSbSe_2$, Tl_9SbSe_6 and Tl_5SbSe_4 formed congruently at 748 and 743 and incongruently at 628 K, respectively. However, the following compounds with the compositions $TlSb_3Se_5$, $TlSbSe_2$ andTl_9SbSe_6 have been found in this system by authors of [51]. The former two compounds melt peritectically whereas the latter one is reported congruent melting. According to Ref. [52], Tl_9SbSe_6 and $TlSbSe_2$ melt congruently while $TlSb_3Se_5$ melts incongruent. The authors of [52] have also found the two immiscibility areas, covering the range of compositions 22-31 and 80-90 mol % Sb_2Se_3. However, the presence of these immiscibility areas is not confirmed in [53,54], in which the two thallium-antimony selenide melt congruently at 750 K ($TlSbSe_2$) and 740 K (Tl_9SbSe_6), and two ones melt with the decomposition on the peritectic reaction at 740 K ($TlSb_3Se_5$) and 625 K (Tl_5SbSe_4). An updated version of the T-x diagram of the Tl_2Se-Sb_2Se_3 system, reported in [53] shown in Fig. 1. According to this diagram, the compound with a composition Tl_3SbSe_3 melts at 625 K incongruently and has a phase transition at 575 K. In a recently published work [55] for this compound composition confirmed as $Tl_{26}Sb_4Se_{19}$.

In [52,56,57] two versions of the complete the T-x-y diagram of the Tl-Sb-Se system are presented. According to [52], besides the above mentioned compounds, there are also Tl_2SbSe_2, Tl_3SbSe_2, Tl_4SbSe_2, located on the quasi-binary section $TlSbSe_2$-Tl, and $Tl_6Sb_8Se_{12}$. These compounds have not been confirmed in [57] (Fig. 2), according to isopleth section $TlSbSe_2$-Tl is not a quasi-binary and crosses quasi-binary section Tl_2Se-Sb, Tl_9SbSe_6-Sb and stable in the subsolidus section Tl_3SbSe_3-Sb. Alloys with compositions Tl_4SbSe_2, Tl_3SbSe_2 and Tl_2SbSe_2 reported in [52] as the ternary compounds, correspond to points of intersection of the above pointed sections and are two-phase mixtures: Tl_2Se+Sb, Tl_9SbSe_6+Sb and Tl_3SbSe_3+Sb. Other "compounds", found in [52] ($Tl_6Sb_8Se_{12}$) also consists of a two-phase mixture $TlSbSe_2$+Se [56].

3.2 The Tl-Bi-Se System

The quasibinary section of Tl_2Se-Bi_2Se_3 investigated in [58,59]. According to [58], it is characterized by the formation of two congruently melting ternary compounds: $TlBiSe_2$ (980 K) and Tl_9BiSe_6 (785 K). Repeated research [59] confirmed the data of [58] and showed that Tl_9BiSe_6 forms a continuous series of solid solutions with Tl_2Se (δ-phase). Authors [60] using a result of the DTA suggest the formation of the ternary phase with the composition $Tl_{0,78}Bi_{1,07}Se_2$. A T-x-y phase diagram of the Tl-Bi-Se was constructed in [61] (Fig. 2).

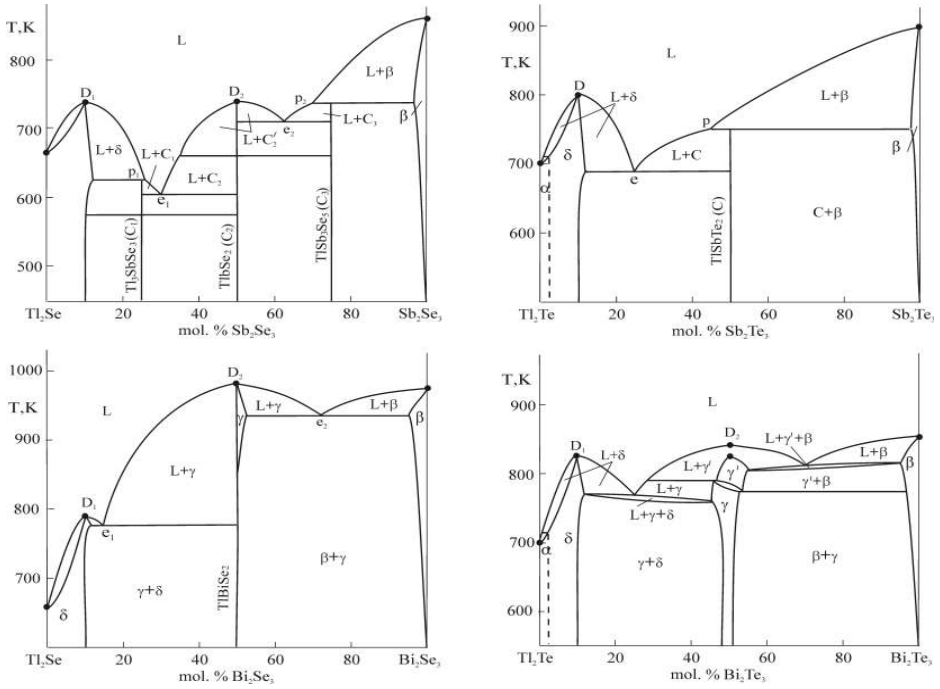

Fig. 1. Phase diagrams of Tl_2Se-Sb_2Se_3 [53], Tl_2Te-Sb_2Te_3 [65], Tl_2Se-Bi_2Se_3 [59], Tl_2Te-Bi_2Te_3 [69] systems

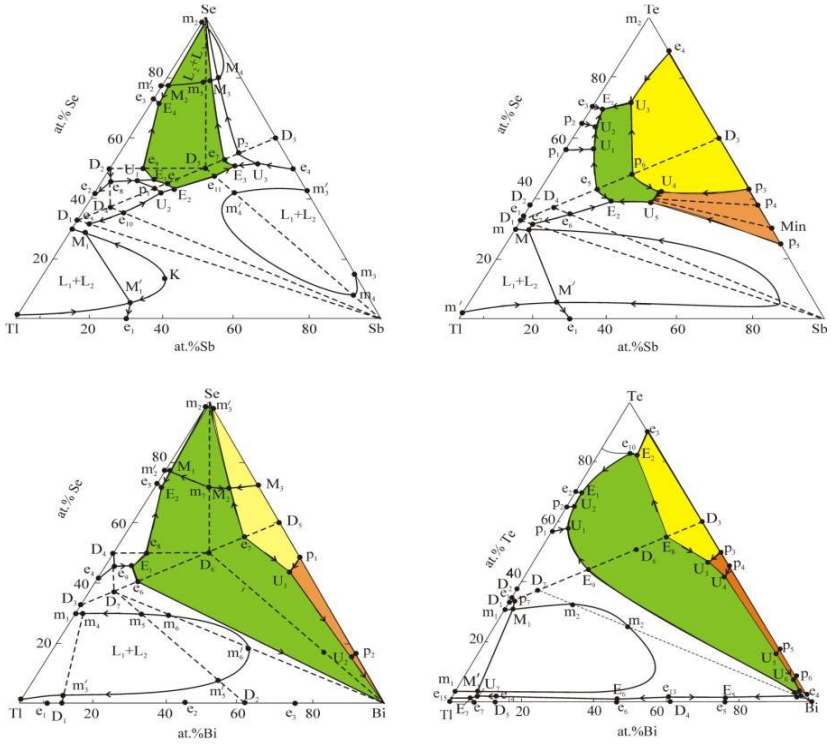

Fig. 2. Liquidus surface projections of Tl-Sb-Se [57], Tl-Sb-Te [65], Tl-Bi-Se [61] and Tl-Bi-Te [69] systems. The dotted line – are quasibinary sections. The primary crystallization areas of Tis phases are colored

3.3 The Tl-Sb-Te System

The quasibinary section Tl_2Te-Sb_2Te_3 is characterized by the formation of two ternary compounds Tl_9SbTe_6 and $TlSbTe_2$ that melt congruently at 798 K and incongruently at 753 K, respectively [62]. In [63-65] this system has studied entirely. Data of [62] on a Tl_2Te-Sb_2Te_3 section (Fig. 1) are confirmed in [64,65]. In [65] the isothermal section and the liquidus surface projection of the Tl-Sb-Te system are constructed (Fig. 2).

3.4 The Tl-Bi-Te System

The phase diagram of the Tl_9BiTe_6-Bi_2Te_3 section is constructed in [66]. It is shown that the compounds Tl_9BiTe_6 and $TlBiTe_2$ melt congruently at 830 and 850 K, respectively. The Tl_2Te-Bi_2Te_3 section is studied [67], and data of [66] are confirmed. In addition it was shown that Tl_9BiTe_6 forms with Tl_2Te-type a limited solid solutions series with morphotropic phase transition. According to [68] the $TlBiTe_2$ compound melts incongruently at 793K, and the distectic maximum according to another phase with composition $Tl_{0,83}Bi_{1,06}Te_2$. In [69], authors show that $TlBiTe_2$ melt incongruently at 788K. Besides reported ternary compounds the new phase $Tl_{0,8}Bi_{1,2}Te_2$ with congruent melting at 815 K was discovered. Authors of [70] showed the complete *T-x-y* diagram of the Tl-Bi-Te system (Fig. 2) and a new version of its isopleth section Tl_2Te-Bi_2Te_3 (Fig. 1). It was found [70] that the Tl_2Te-Bi_2Te_3 section, unlike other sections of Tl_2X-B_2X_3 types, is no quasibinary (Fig. 1). This is due to a noticeable (~ 5 at.%) deviation of distectic point from the stoichiometric composition $TlBiTe_2$.

Thermodynamic properties of ternary phases in the Tl-B^V-X systems, including $TlBVX_2$ compounds were studied in a number of research works experimentally by EMF technique [54,57,58,63,70-72].

Thus, the phase equilibria in the ternary Tl-B^V-X systems were established via consecutive studies of various research teams and the latest versions of their phase diagrams can be considered reliable enough.

Compounds TlB^VX_2, and phases based on binary compounds $B^V{}_2X_3$ possess TIs properties and have vast areas of primary crystallization both on quasi-binary sections Tl_2X-$B^V{}_2X_3$ (Fig.1), and on T-x-y diagrams (Fig. 2). Therefore, their single crystals can be grown from melts of various compositions both on indicated sections and on areas of primary crystallization on the T-x-y diagrams.

4. QUATERNARY SYSTEMS COMPOSED BY BINARY CHALCOGENIDES OF Tl, Sb AND Bi

A series of works [73-84] present the results of studies of phase equilibria in quaternary Tl-Sb-Bi-Se (Te) and Tl-Sb(Bi)-X-X^I (X, X^I - S, Se, Te) systems on quasiternary (Tl_2X-Sb_2X_3-Bi_2X_3) and ternary reciprocal ($3Tl_2X + B^V_2X^I_3 \leftrightarrow 3Tl_2X^I + B^V_2X_3$) planes. In these studies the primary crystallization field of nonstoichiometric phases based on ternary TlB^VX_2 and binary $B^V_2X_3$ compounds were specified, that can be used for growing their single crystals.

Below, the isopleth TlB^VX_2-$TlB^VX^I_2$ and $TlSbX_2$-$TlBiX_2$ (Fig. 3) as well as isothermal sections at 300 K of the phase diagram (Figs. 4, 5) and liquidus surfaces projection of some of these systems (Figs. 4,6) were represented.

As it can be seen from Fig. 3, the sulfide-selenide systems are quasi-binary, and the system comprising the compounds $TlSbTe_2$ and $TlBiTe_2$ are no qausibinary due to incongruent melting character of the $TlSbTe_2$ and significant deviation distectic point of the $TlBiTe_2$ from the stoichiometric composition.

All eight considered systems are characterized by the formation of wide or continuous substitutional solid solutions. Should be noted that in $TlBiTe_2$ including systems the compositions of solid solutions based on this compound might be little bit shifted from the T-x plane.

Solid phase equilibria diagrams (Figs. 3, 4) demonstrate the homogeneity region of solid solutions based on binary and ternary compounds, in particular TlB^VX_2 and their heterogeneous equilibria with each other. It is evident that the field of solid solutions based on TlB^VX_2 and $B^V_2X_3$ and possessing TI properties, located along sections TlB^VX_2-$TlB^VX^I_2$, $TlSbX_2$-$TlBiX_2$ and boundary $B^V{}_2X_3$ -$B^V{}_2X^I_3$ and Sb_2X_3-Bi_2X_3 systems as narrow strips.

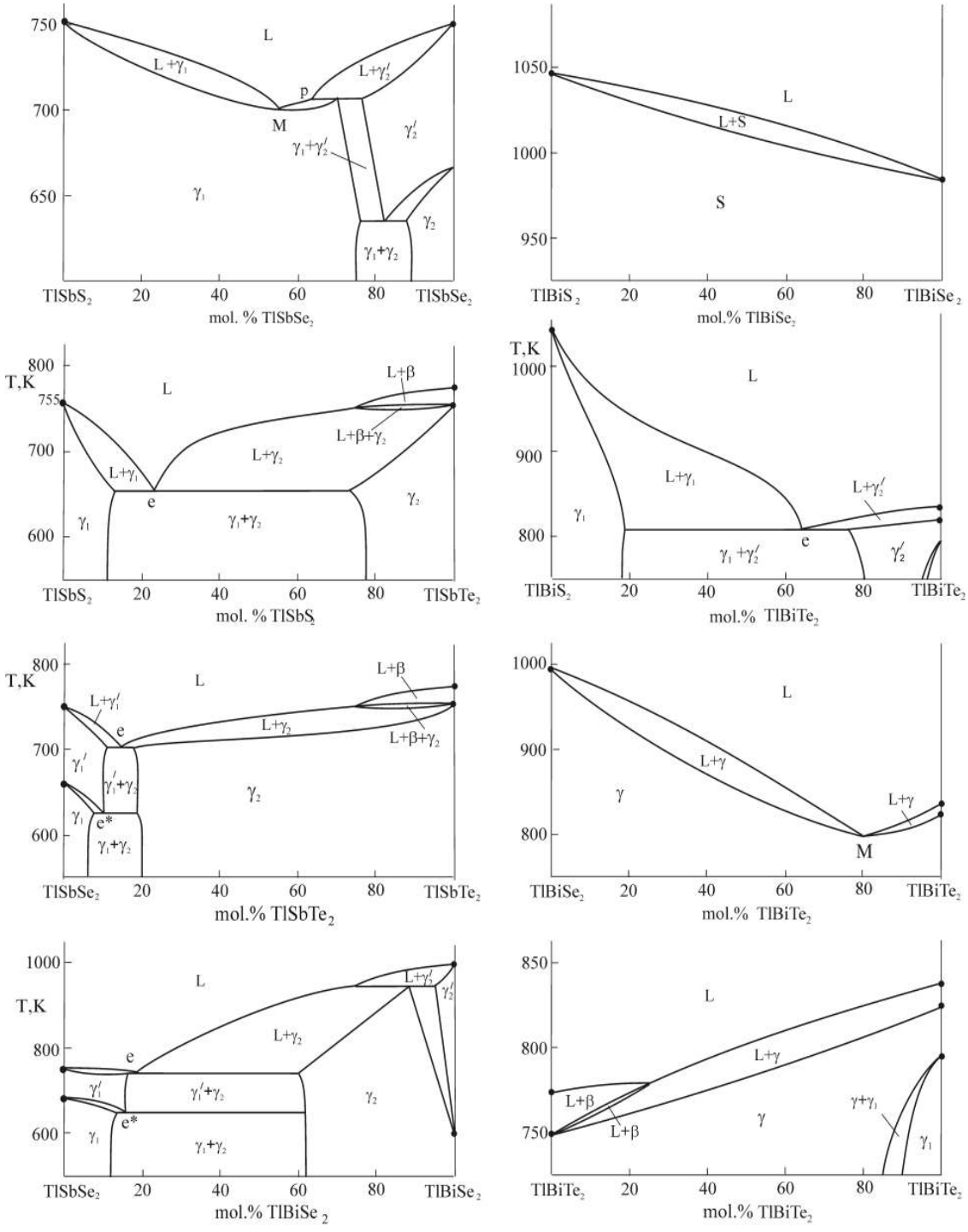

Fig. 3. Phase diagrams of $TlSbS_2$-$TlSbSe_2$ [75],$TlBiS_2$-$TlBiSe_2$ [76],$TlSbS_2$-$TlSbTe_2$ [78], $TlBiS_2$-$TlBiTe_2$ [83], $TlSbSe_2$-$TlSbTe_2$ [80], $TlBiSe_2$-$TlBiTe_2$ [84] ,$TlSbSe_2$-$TlBiSe_2$ [73], $TlSbTe_2$-$TlBiTe_2$ [74] systems

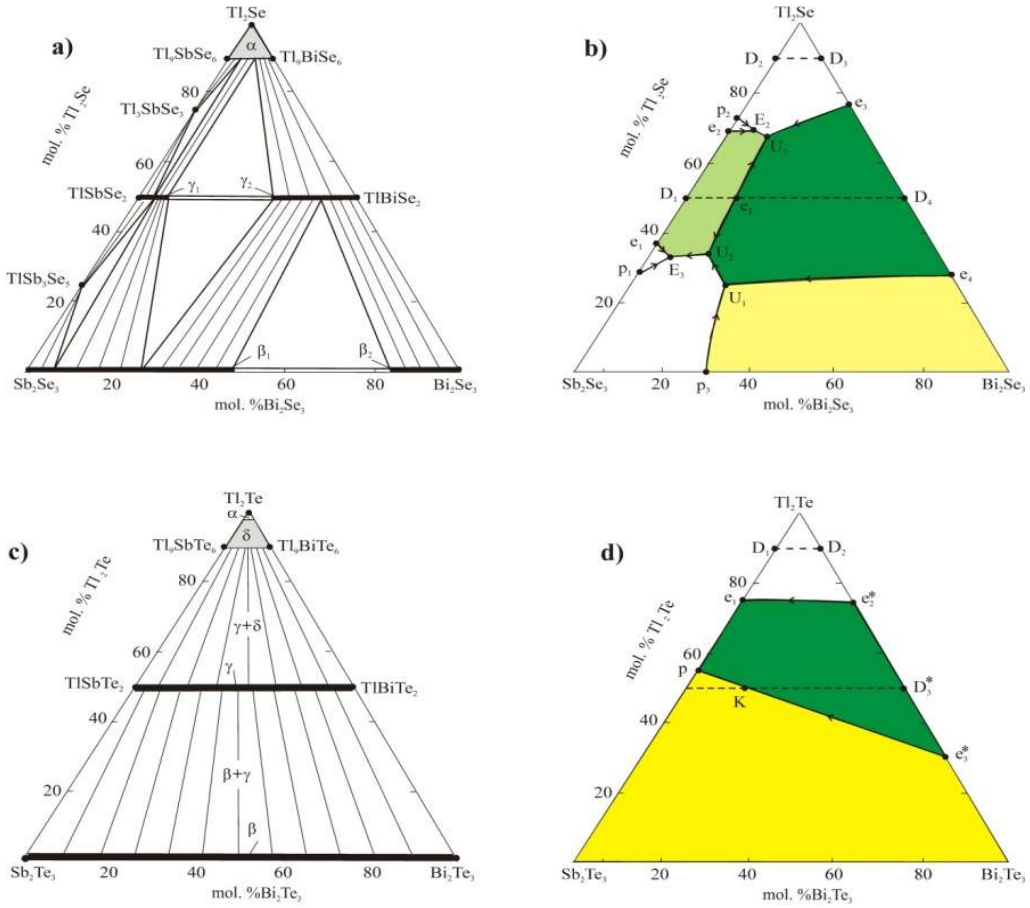

Fig. 4. Solid-phase equilibria diagrams and liquidus surface projections of Tl_2Se-Sb_2Se_3-Bi_2Se_3 [73] and Tl_2Te-Sb_2Te_3-Bi_2Te_3 [74] systems. the primary crystallization areas of potential TIs phases are colored

Liquidus surface projection of systems mentioned above (Figs. 4, 6) demonstrate the field of primary crystallization of phases, in particular solid solutions based on $TlBVX_2$ and $B_2^V X_3$. Fields of primary crystallization of phases, which are potential TIs materials, painted green (phases based on TlB^VSe_2 and TlB^VTe_2) and yellow (phases based on Bi_2Se_3, Sb_2Te_3 and Bi_2Te_3) on Figs. 4 and 6.

5. THE CRYSTAL STRUCTURES OF THALLIUM-BASED TIs

The crystal structure data and features of the TlB^VX_2 compounds and solid solutions series based on them have been studied in [85-87] and reviewed in detail by Cava et al. [88]. The TlB^VX_2 compounds are crystallized in rhombohedral crystal system R-3m (#166). Fig. 7 show the crystal structure of the compounds $TlBiSe(Te)_2$. The metal atoms are arranged in the following positions: Tl 3a (0,0,0); Bi 3b (0,0,0.5); and anions in position with one variable coordinates: Se, Te or 6c (0,0,0.25). The unit cell parameters are: ***a*** = 4,24 Å (Se), ***a***= 4.527 Å (Te), c = 22.330 Å (Se), and 23,118 Å (Te). Cubic close-packed (-A-B-C-A-B-C-) layers (Fig. 7) alternate in the following order: –(Se,Te)–Bi–(Se,Te)–Tl–. Despite the lack van der Waals bonds, these crystals are very well cleaved along planes (001), in which topological surface states is found. However, until recently, experimentally verified data on structure of the split surface is absent. The authors of [40,88] studied cleaved surface of the $TlBiSe_2$ by scanning tunneling microscopy (STM) and photoelectron spectroscopy of basic levels (CL-PES) have concluded that the thallium atoms create islets over the layers of atoms Se, covering the last half.

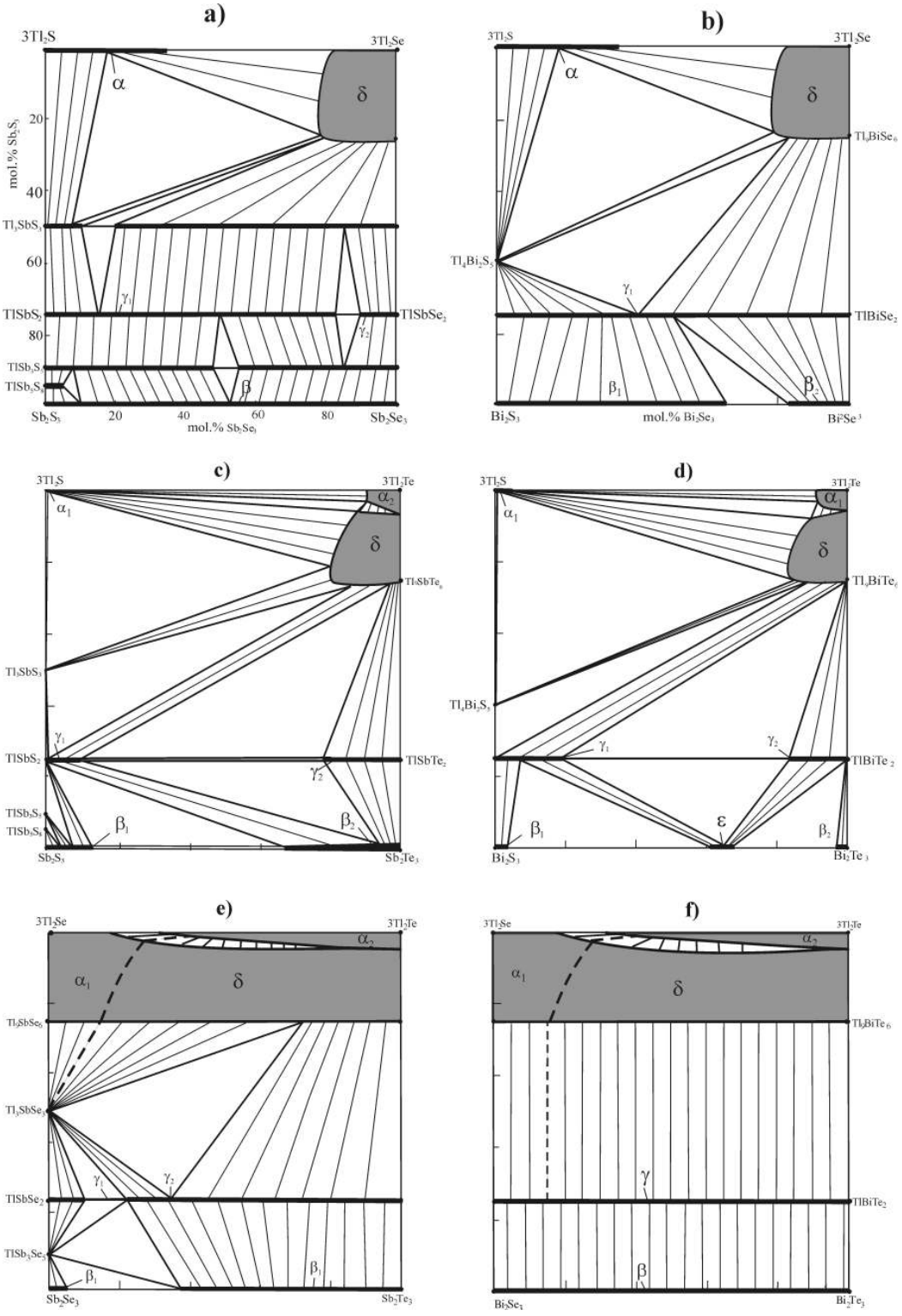

Fig. 5. Solid-phase equilibria diagrams of reciprocal systems

(a) $3Tl_2S+Sb_2Se_3 \leftrightarrow 3Tl_2Se+Sb_2S_3$ [75]; (b) $3Tl_2S+Bi_2Se_3 \leftrightarrow 3Tl_2Se+Bi_2S_3$ [76]; (c) $3Tl_2S+Sb_2Te_3 \leftrightarrow 3Tl_2Te+Sb_2S$ [78]; (d) $3Tl_2S+Bi_2Te_3 \leftrightarrow 3Tl_2Te+Bi_2S_3$ [83]; (e) $3Tl_2Se+Sb_2Te_3 \leftrightarrow 3Tl_2Te+Sb_2Se_3$ [80]; (f) $3Tl_2Se+Bi_2Te_3 \leftrightarrow 3Tl_2Te+Bi_2Se_3$ [84]

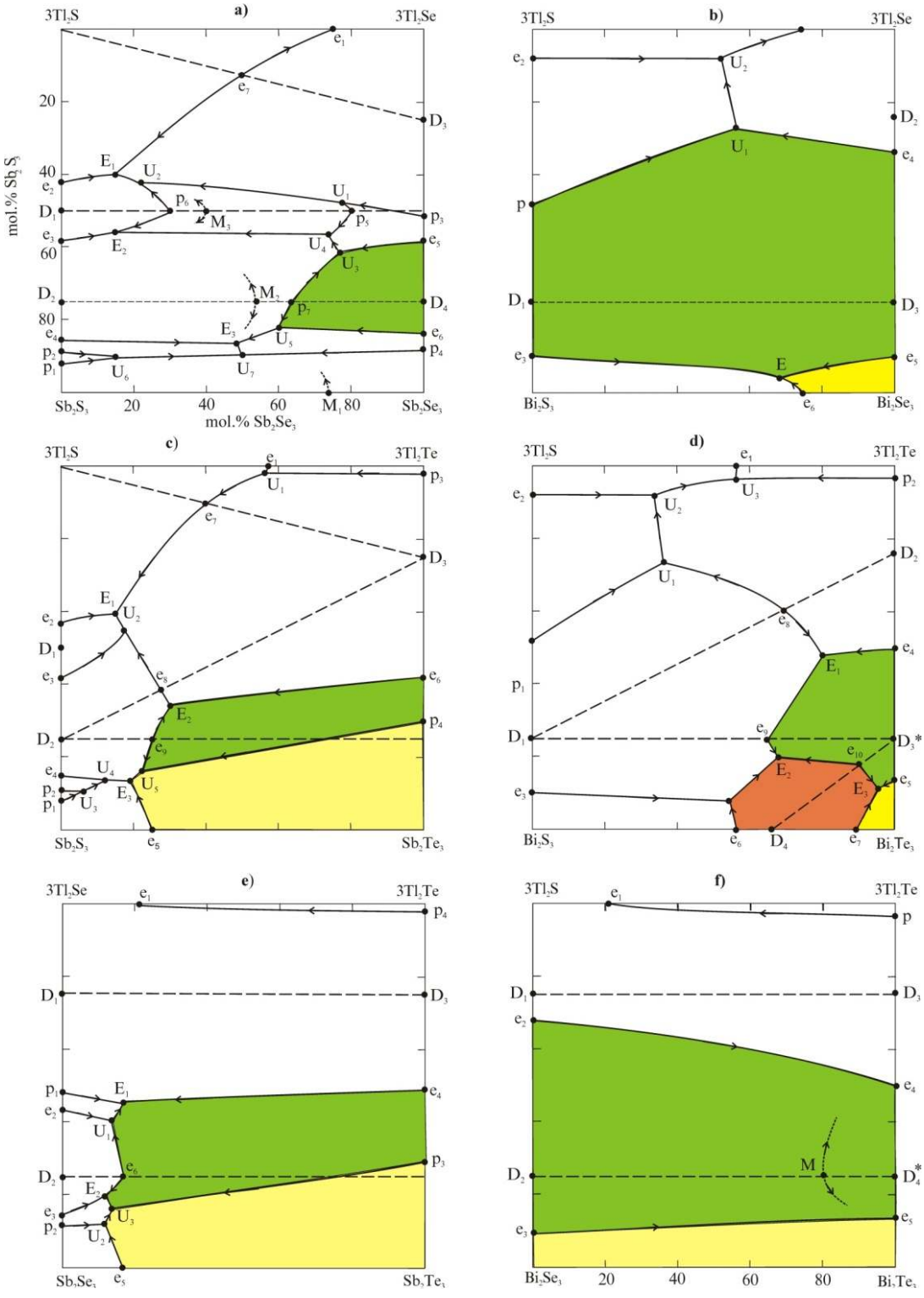

Fig. 6. Liquidus surface projections of the reciprocal systems

(a) $3Tl_2S+Sb_2Se_3 \leftrightarrow 3Tl_2Se+Sb_2S_3$ [75]; (b) $3Tl_2S+Bi_2Se_3 \leftrightarrow 3Tl_2Se+Bi_2S_3$ [76]; (c) $3Tl_2S+Sb_2Te_3 \leftrightarrow 3Tl_2Te+Sb_2S$ [78]; (d) $3Tl_2S+Bi_2Te_3 \leftrightarrow 3Tl_2Te+Bi_2S_3$ [83]; (e) $3Tl_2Se+Sb_2Te_3 \leftrightarrow 3Tl_2Te+Sb_2Se_3$ [80]; (f) $3Tl_2Se+Bi_2Te_3 \leftrightarrow 3Tl_2Te+Bi_2Se_3$ [84], the primary crystallization areas of potential TIs phases are colored

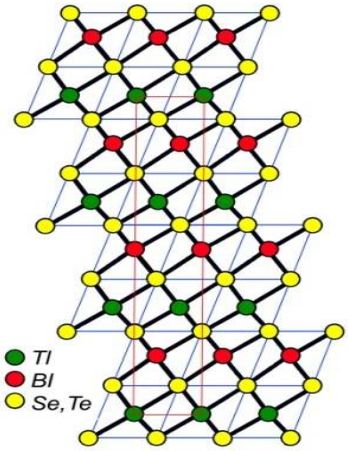

Fig. 7. The crystal structure of the $TlBiSe_2$ and $TlBiTe_2$

6. CONCLUSION

A new class of functional materials – topological insulators - due to its unusual physical properties is extremely promising for a various applications ranging from spintronics and quantum computing to medicine and security systems. Therefore, one of many interdisciplinary problems of chemistry and materials science is a significant expansion of the range of investigated materials by development of new compounds and alloys based on them using phase diagrams of the corresponding systems.

Our literature survey has shown, that the phase equilibria in the ternary Tl-B^V-Se(Te) systems, as well as in quasiternary Tl_2X-Sb_2X_3-Bi_2X_3 and reciprocal $3Tl_2X+B^V{}_2X^I{}_3 \leftrightarrow 3Tl_2X^I+B^V{}_2X_3$ systems studied in detail. Constructed complete T-x-y diagram of these systems and their various isopleth and isothermal sections offer ample opportunities for growth of single crystals in ternary and more complex phases.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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