

CHEMISTRY OF THALLIUM-BASED TOPOLOGICAL INSULATORS

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 TI-B^V-X (B^V – Sb, Bi; X – Se, Te) systems having TIB^VX₂ type compounds which exhibit spin polarized topological surface state is evaluated and compiled. Published data on the phase equilibria in the quaternary TI-Sb-Bi-X and TI-BV-X-X' systems are also reviewed and it has been revealed that their quasiternary TI₂X-Sb₂X₃-Bi₂X₃ and reciprocal 3TI₂X+B^V₂X₃↔3TI₂X'+B^V₂X₃ subsystems form a wide range of solid solutions based on compounds TIB^VX₂ and B^V₂X₃, 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.

1. INTRODUCTION

In last few years, tetradymite-like binary and ternary layered chalcogenides of bismuth and antimony are as well as some TI-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 Bi₂Se₃, Bi₂Te₃, Sb₂Te₃ [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 TiB^VX_2 type also exhibit the TIs properties [31-34].

The development of magnetism in TIs 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 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 $Ti-B^V-X$ (B^V -Sb, Bi; X-Se, Te) and quaternary $Ti-Sb-Bi-X$, $Ti-B^V-X-X'$ 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 $Ti-B^V-X$ (B^V -Sb, Bi; X-Se, Te) SYSTEMS

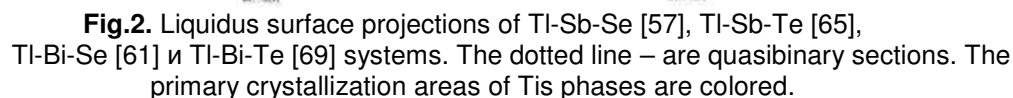
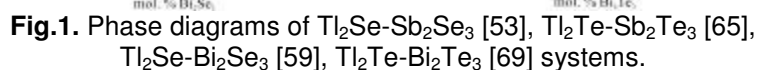
In ternary $Ti-B^V-X$ systems thermodynamically stable phases formed on certain quasibinary section. Therefore, for the preparation of single crystals of many ternary compounds, the T - x diagrams of the corresponding quasi-binary systems are often used. More comprehensive information on the character 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.

92 Phase equilibria in the $\text{TI-B}^{\text{V}}\text{-X}$ systems have been reported in numerous research works
 93 [50-69].

94 **The TI-Sb-Se system.** The quasibinary section $\text{TI}_2\text{Se-Sb}_2\text{Se}_3$ of this system studied in [50-
 95 55]. According to Ref. [50], three ternary compounds, namely TISbSe_2 , TI_9SbSe_6 and
 96 TI_5SbSe_4 formed congruently at 748 and 743 and incongruently at 628 K, respectively.
 97 However, the following compounds with the compositions $\text{TI}_3\text{Sb}_3\text{Se}_5$, TISbSe_2 and TI_9SbSe_6
 98 have been found in this system by authors of [51]. The former two compounds melt
 99 peritectically whereas the latter one is reported congruent melting. According to Ref. [52],
 100 TI_9SbSe_6 and TISbSe_2 melt congruently while $\text{TI}_3\text{Sb}_3\text{Se}_5$ melts incongruent. The authors of
 101 [52] have also found the two immiscibility areas, covering the range of compositions 22-31
 102 and 80-90 mol % Sb_2Se_3 . However, the presence of these immiscibility areas is not
 103 confirmed in [53,54], in which the two thallium-antimony selenide melt congruently at 750 K
 104 (TISbSe_2) and 740 K (TI_9SbSe_6), and two ones melt with the decomposition on the peritectic
 105 reaction at 740 K ($\text{TI}_3\text{Sb}_3\text{Se}_5$) and 625 K (TI_5SbSe_4). An updated version of the T-x diagram
 106 of the $\text{TI}_2\text{Se-Sb}_2\text{Se}_3$ system, reported in [53] shown in Fig.1. According to this diagram, the
 107 compound with a composition TI_3SbSe_3 melts at 625 K incongruently and has a phase
 108 transition at 575 K. In a recently published work [55] for this compound composition
 109 confirmed as $\text{TI}_{26}\text{Sb}_4\text{Se}_{19}$.

110 In [52,56,57] two versions of the complete the T-x-y diagram of the TI-Sb-Se system are
 111 presented. According to [52], besides the above mentioned compounds, there are also
 112 TI_2SbSe_2 , TI_3SbSe_2 , TI_4SbSe_2 , located on the quasi-binary section $\text{TISbSe}_2\text{-TI}$, and
 113 $\text{TI}_6\text{Sb}_8\text{Se}_{12}$. These compounds have not been confirmed in [57] (Fig. 2), according to isopleth
 114 section $\text{TISbSe}_2\text{-TI}$ is not a quasi-binary and crosses quasi-binary section $\text{TI}_2\text{Se-Sb}$,
 115 $\text{TI}_9\text{SbSe}_6\text{-Sb}$ and stable in the subsolidus section $\text{TI}_3\text{SbSe}_3\text{-Sb}$. Alloys with compositions
 116 TI_4SbSe_2 , TI_3SbSe_2 and TI_2SbSe_2 reported in [52] as the ternary compounds, correspond to
 117 points of intersection of the above pointed sections and are two-phase mixtures: $\text{TI}_2\text{Se+Sb}$,
 118 $\text{TI}_9\text{SbSe}_6\text{+Sb}$ and $\text{TI}_3\text{SbSe}_3\text{+Sb}$. Other "compounds", found in [52] ($\text{TI}_6\text{Sb}_8\text{Se}_{12}$) also consists
 119 of a two-phase mixture $\text{TISbSe}_2\text{+Se}$ [56].

120 **The TI-Bi-Se system.** The quasibinary section of $\text{TI}_2\text{Se-Bi}_2\text{Se}_3$ investigated in [58,59].
 121 According to [58], it is characterized by the formation of two congruently melting ternary
 122 compounds: TIBiSe_2 (980 K) and TI_9BiSe_6 (785 K). Repeated research [59] confirmed the
 123 data of [58] and showed that TI_9BiSe_6 forms a continuous series of solid solutions with TI_2Se
 124 (δ -phase). Authors [60] using a result of the DTA suggest the formation of the ternary phase
 125 with the composition $\text{TI}_{0.78}\text{Bi}_{1.07}\text{Se}_2$. A T-x-y phase diagram of the TI-Bi-Se was constructed
 126 in [61] (Fig.2).



The TI-Sb-Te system. The quasibinary section $\text{Ti}_2\text{Te-Sb}_2\text{Te}_3$ is characterized by the formation of two ternary compounds Ti_9SbTe_6 and TiSbTe_2 that melt congruently at 798 K and incongruently at 753 K, respectively [61]. In [62-64] this system has studied entirely. Data of [61] on a $\text{Ti}_2\text{Te-Sb}_2\text{Te}_3$ section (Fig.1) are confirmed, as well as the isothermal section and the liquidus surface projection of the TI-Sb-Te system is constructed (Fig. 2).

The TI-Bi-Te system. The phase diagram of the $\text{Ti}_9\text{BiTe}_6\text{-Bi}_2\text{Te}_3$ section is constructed in [65]. It is shown that the compounds Ti_9BiTe_6 and TiBiTe_2 melt congruently at 830 and 850 K, respectively. The $\text{Ti}_2\text{Te-Bi}_2\text{Te}_3$ section is studied [66], and data of [65] are confirmed. In addition it was shown that Ti_9BiTe_6 forms with Ti_2Te -type a limited solid solutions series with morphotropic phase transition. According to [67] the TiBiTe_2 compound melts incongruently at 793K, and the distectic maximum according to another phase with composition $\text{Ti}_{0.83}\text{Bi}_{1.06}\text{Te}_2$. In [68], authors show that TiBiTe_2 melt incongruently at 788K. Besides reported ternary compounds the new phase $\text{Ti}_{0.8}\text{Bi}_{1.2}\text{Te}_2$ with congruent melting at 815 K was discovered. Authors of [69] showed the complete T - x - y diagram of the TI-Bi-Te system (Fig. 2) and a new version of its isopleth section $\text{Ti}_2\text{Te-Bi}_2\text{Te}_3$ (Fig.1). It was found [69] that the $\text{Ti}_2\text{Te-Bi}_2\text{Te}_3$ section, unlike other sections of $\text{Ti}_2\text{X-B}_2\text{X}_3$ types, is no quasibinary (Fig. 1). This is due to a noticeable (~ 5 at.%) deviation of distectic point from the stoichiometric composition TiBiTe_2 .

Thermodynamic properties of ternary phases in the $\text{Ti-B}^{\text{V}}\text{-X}$ systems, including TIBVX_2 compounds were studied in a number of research works experimentally by EMF technique [54,57,58,62,70-72].

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

Compounds $\text{TIB}^{\text{V}}\text{X}_2$, and phases based on binary compounds $\text{B}_2^{\text{V}}\text{X}_3$ possess TIs properties and have vast areas of primary crystallization both on quasi-binary sections $\text{Ti}_2\text{X-B}_2^{\text{V}}\text{X}_3$ (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 TI, Sb AND Bi

A series of works [73-84] present the results of studies of phase equilibria in quaternary TI-Sb-Bi-Se (Te) and TI-Sb(Bi)-X-X' (X, X' - S, Se, Te) systems on quasiternary ($\text{Ti}_2\text{X-Sb}_2\text{X}_3\text{-Bi}_2\text{X}_3$) and ternary reciprocal ($3\text{Ti}_2\text{X} + \text{B}_2^{\text{V}}\text{X}_3 \leftrightarrow 3\text{Ti}_2\text{X}' + \text{B}_2^{\text{V}}\text{X}_3$) planes. In these studies the primary crystallization field of nonstoichiometric phases based on ternary $\text{TIB}^{\text{V}}\text{X}_2$ and binary $\text{B}_2^{\text{V}}\text{X}_3$ compounds were specified, that can be used for growing their single crystals.

Below, the isopleth $\text{TIB}^{\text{V}}\text{X}_2\text{-TIB}^{\text{V}}\text{X}'_2$ and $\text{TISbX}_2\text{-TiBiX}_2$ (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 TISbTe_2 and TiBiTe_2 are no qausibinary due to incongruent melting character of the TISbTe_2 and significant deviation distectic point of the TiBiTe_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 TiBiTe_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 $\text{TIB}^{\text{V}}\text{X}_2$ and their heterogeneous equilibria with each other. It is evident that the field of solid solutions based

on TiB^VX_2 and $B_2^VX_3$ and possessing TI properties, located along sections TiB^VX_2 - $TiB^VX'_2$, $TiSbX_2$ - $TiBiX_2$ and boundary $B_2^VX_3$ - $B_2^VX'_3$ and Sb_2X_3 - Bi_2X_3 systems as narrow strips. Liquidus surface projection of systems mentioned above (Figs. 4, 6) demonstrate the field of primary crystallization of phases, in particular solid solutions based on $TiBVX_2$ and $B_2^VX_3$. Fields of primary crystallization of phases, which are potential TIs materials, painted green (phases based on TiB^VSe_2 and TiB^VTe_2) and yellow (phases based on Bi_2Se_3 , Sb_2Te_3 and Bi_2Te_3) on Figs. 4 and 6.

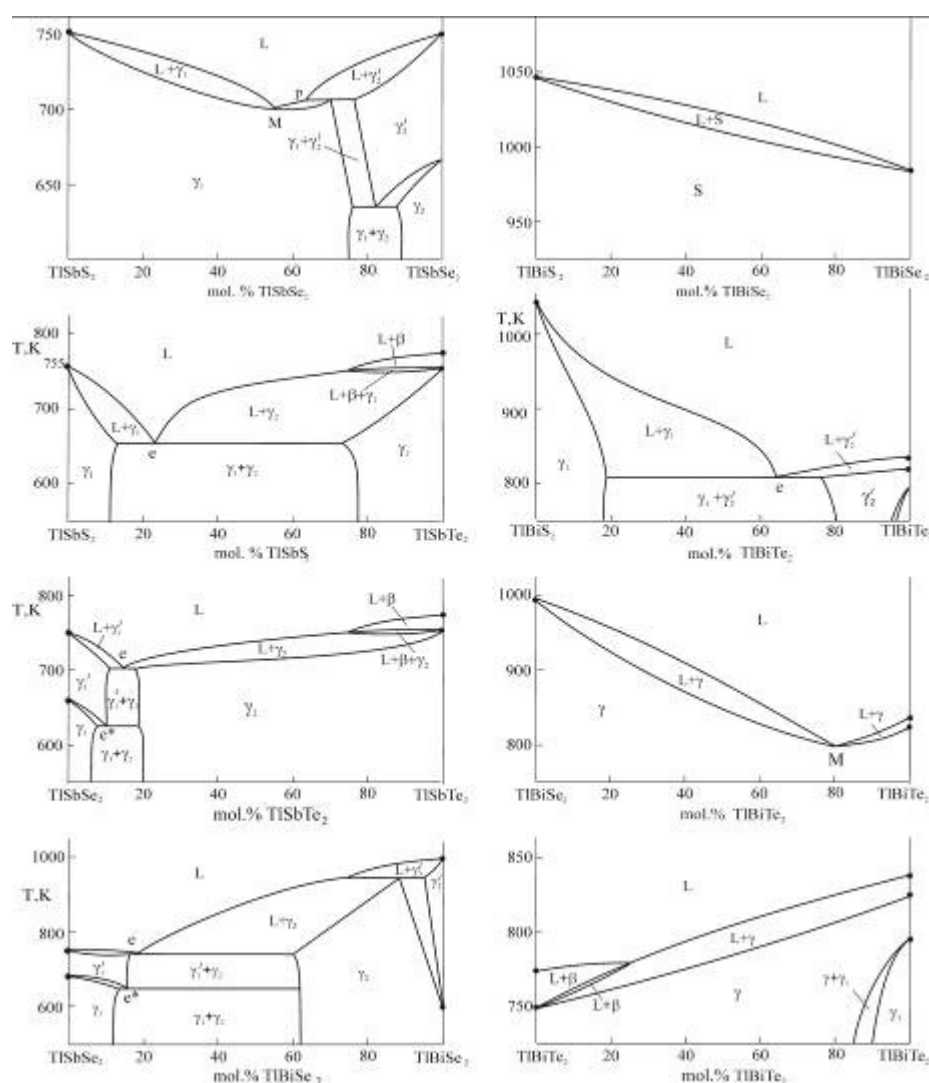
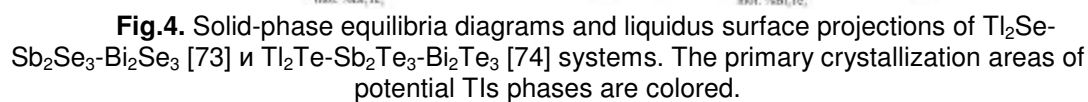


Fig.3. Phase diagrams of $TiSbS_2$ - $TiSbSe_2$ [75], $TiBiS_2$ - $TiBiSe_2$ [76], $TiSbS_2$ - $TiSbTe_2$ [78], $TiBiS_2$ - $TiBiTe_2$ [83], $TiSbSe_2$ - $TiSbTe_2$ [80], $TiBiSe_2$ - $TiBiTe_2$ [84], $TiSbSe_2$ - $TiBiSe_2$ [73], $TiSbTe_2$ - $TiBiTe_2$ [74] systems.



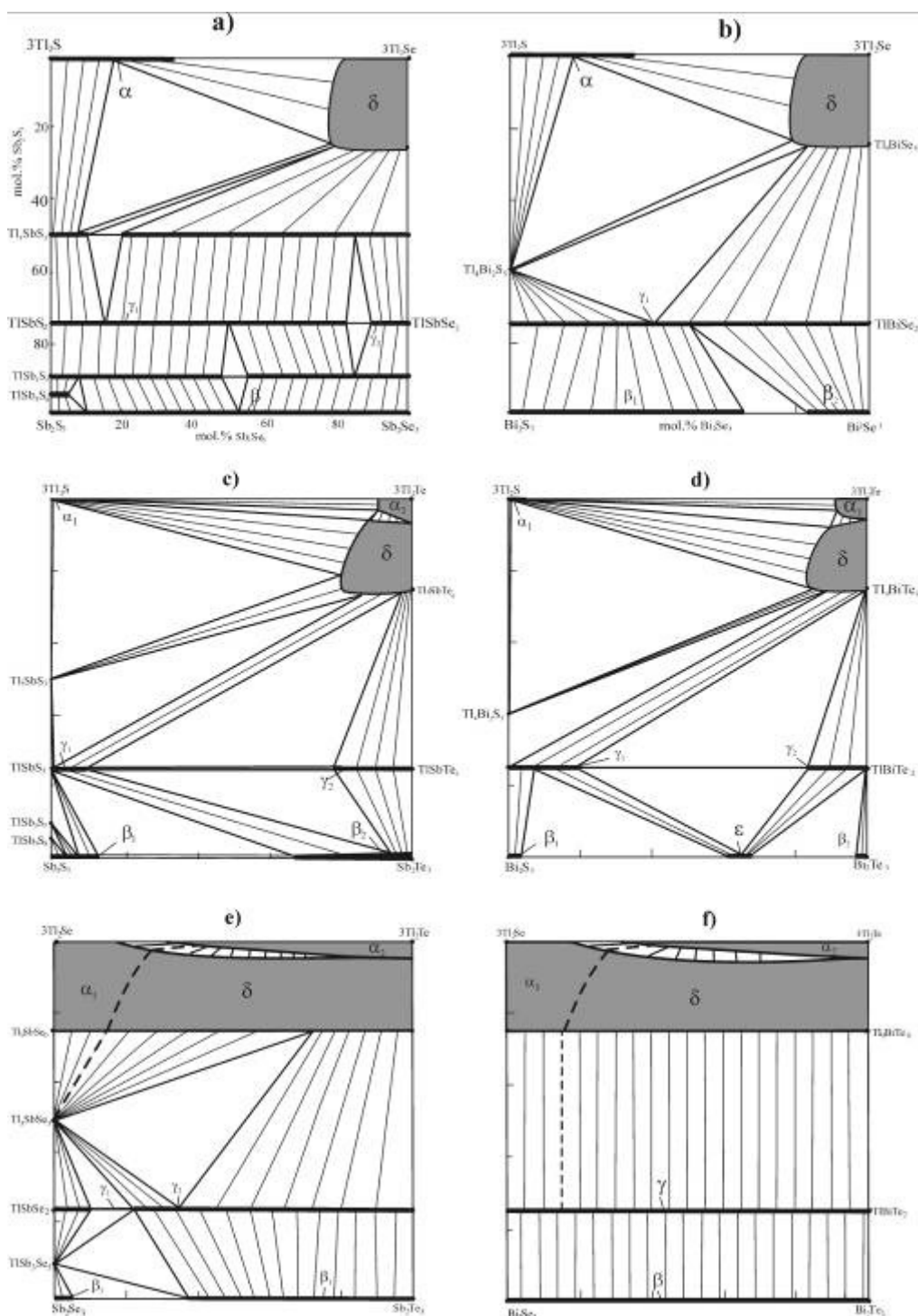


Fig.5. Solid-phase equilibria diagrams of reciprocal systems:
(a) 3Ti₂S+Sb₂Se₃↔3Ti₂Se+Sb₂S₃ [75]; (b) 3Ti₂S+Bi₂Se₃↔3Ti₂Se+Bi₂S₃ [76];
(c) 3Ti₂S+Sb₂Te₃↔3Ti₂Te+Sb₂S₃ [78]; (d) 3Ti₂S+Bi₂Te₃↔3Ti₂Te+Bi₂S₃ [83];
(e) 3Ti₂Se+Sb₂Te₃↔3Ti₂Te+Sb₂Se₃ [80]; (f) 3Ti₂Se+Bi₂Te₃↔3Ti₂Te+Bi₂Se₃ [84].

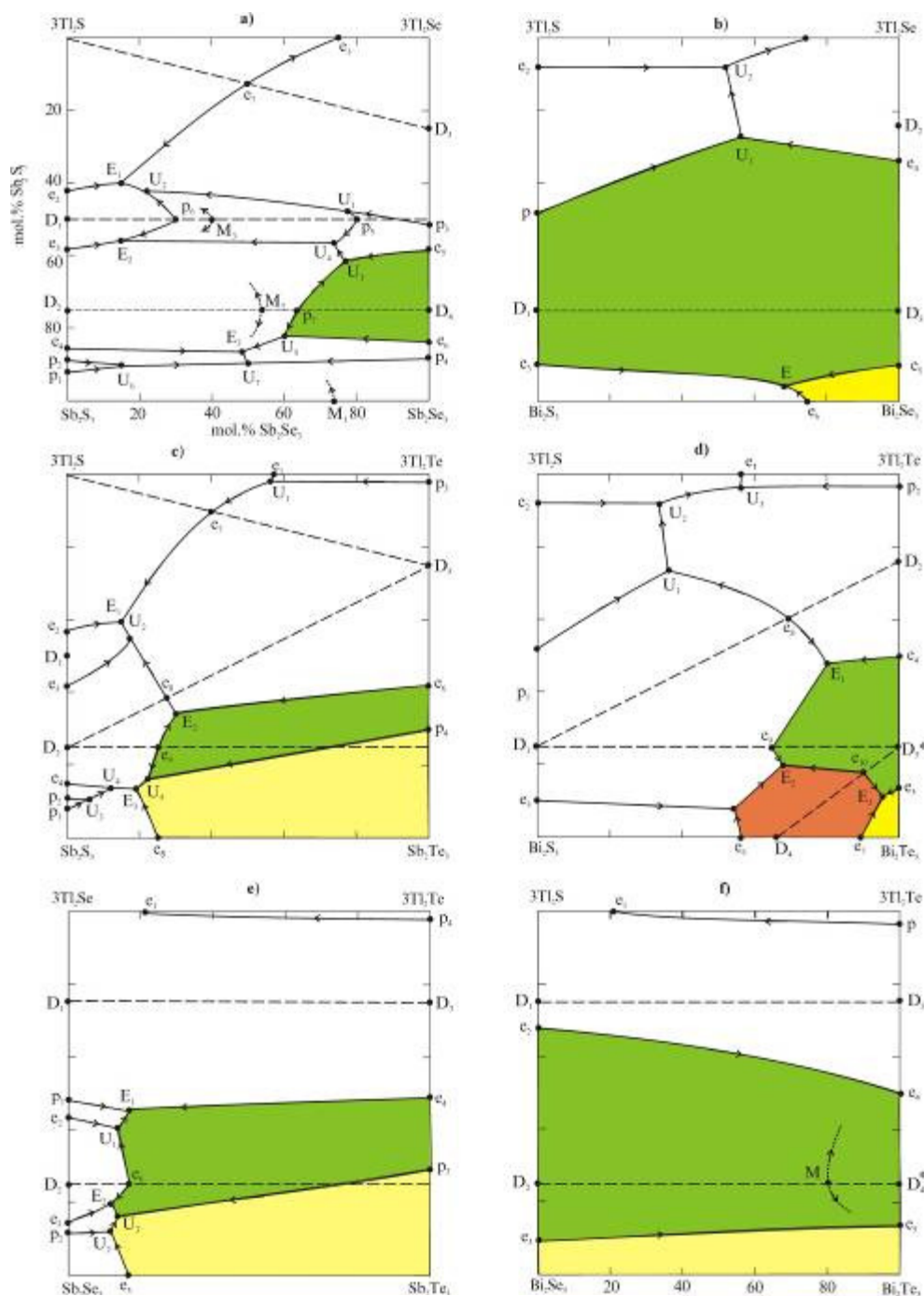


Fig.6. Liquidus surface projections of the reciprocal systems:
(a) $3\text{Tl}_2\text{S} + \text{Sb}_2\text{Se}_3 \leftrightarrow 3\text{Tl}_2\text{Se} + \text{Sb}_2\text{S}_3$ [75]; (b) $3\text{Tl}_2\text{S} + \text{Bi}_2\text{Se}_3 \leftrightarrow 3\text{Tl}_2\text{Se} + \text{Bi}_2\text{S}_3$ [76];
(c) $3\text{Tl}_2\text{S} + \text{Sb}_2\text{Te}_3 \leftrightarrow 3\text{Tl}_2\text{Te} + \text{Sb}_2\text{S}_3$ [78]; (d) $3\text{Tl}_2\text{S} + \text{Bi}_2\text{Te}_3 \leftrightarrow 3\text{Tl}_2\text{Te} + \text{Bi}_2\text{S}_3$ [83];
(e) $3\text{Tl}_2\text{Se} + \text{Sb}_2\text{Te}_3 \leftrightarrow 3\text{Tl}_2\text{Te} + \text{Sb}_2\text{Se}_3$ [80]; (f) $3\text{Tl}_2\text{Se} + \text{Bi}_2\text{Te}_3 \leftrightarrow 3\text{Tl}_2\text{Te} + \text{Bi}_2\text{Se}_3$ [84].
The primary crystallization areas of potential Tl phases are colored.

5. THE CRYSTAL STRUCTURES OF THALLIUM-BASED TIs.

The crystal structure data and features of the $\text{TlBi}^{\text{V}}\text{X}_2$ compounds and solid solutions series based on them have been studied in [85-87] and reviewed in detail by Cava et al. [88]. The $\text{TlBi}^{\text{V}}\text{X}_2$ compounds are crystallized in rhombohedral crystal system R-3m (#166). Fig.7 show the crystal structure of the compounds $\text{TlBiSe}(\text{Te})_2$. 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: $a = 4.24 \text{ \AA}$ (Se), $a = 4.527 \text{ \AA}$ (Te), $c = 22.330 \text{ \AA}$ (Se), and $23.118 \text{ \AA}$ (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.

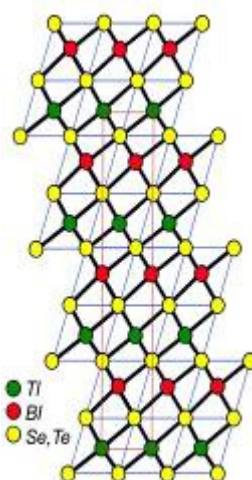


Fig.7. The crystal structure of the TlBiSe_2 and TlBiTe_2

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 $\text{Tl-Bi}^{\text{V}}\text{-Se}(\text{Te})$ systems, as well as in quasiternary $\text{Tl}_2\text{X-Sb}_2\text{X}_3\text{-Bi}_2\text{X}_3$ and reciprocal $3\text{Tl}_2\text{X}+\text{Bi}_2\text{X}_3 \leftrightarrow 3\text{Tl}_2\text{X}'+\text{Bi}_2\text{X}_3$ 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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REFERENCES

1. Kane CL. Condensed matter: An Insulator with a Twist. *Nature Phys.* 2008; 4(5): 348-349.
2. Hasan MZ & Kane CL. Colloquium: Topological Insulators. *Rev.Mod.Phys.* 2010; 82: 3045–3067.
3. Moore JE. The birth of topological insulators. *Nature.* 2010; 464: 194-198
4. Kane CL and Moore JE. Topological insulators. *Physics World.* 2011; 24: 32–36.
5. Pesin D, MacDonald AH. Spintronics and pseudospintronics in graphene and topological insulators. *Nature Mater.* 2012; 11: 409–416
6. Kane CL and Mele EJ. Z₂ Topological Order and the Quantum Spin Hall Effect. *Phys. Rev. Lett.* 2005; 95: 146802
7. Kane CL and Mele EJ. Quantum Spin Hall Effect in Graphene. *Phys. Rev. Lett.* 2005; 95: 226801
8. Xu C and Moore JE. Stability of the quantum spin Hall effect: effects of interactions, disorder, and Z₂ topology. *Phys. Rev.* 2006; B 73: 045322.
9. Moore J.E. and Balents L. Topological invariants of time-reversal-invariant band structures. *Phys. Rev. B.* 2007; 75: 121306
10. Teo JCY, Fu L and Kane CL. Surface states and topological invariants in three-dimensional topological insulators: Application to Bi_{1-x}Sb_x. *Phys. Rev.* 2008; B 78: 045426-15
11. Zhang H, Liu CX, Qi XL, Dai X, Fang Z, Zhang SC. Topological insulators in Bi₂Se₃, Bi₂Te₃ and Sb₂Te₃ with a single Dirac cone on the surface. *Nature physics.* 2009; 5 (6): 438-442
12. Hsieh D, Xia Y, Qian D, Wray L, Meier F, Dil JH et al. Observation of Time-Reversal-Protected Single-Dirac-Cone Topological-Insulator States in Bi₂Te₃ and Sb₂Te₃. *Phys. Rev. Lett.* 2009; 103 (14): 146401.
13. Otrokov MM, Borisova SD, Chis V, Vergniory MG, Ereemeev SV, Kuznetsov VM, Chulkov EV. Efficient step-mediated intercalation of silver atoms deposited on the Bi₂Se₃ surface. *JETP.* 2012; 96(11): 714-718
14. Vergniory MG, Men'shikova TV, Ereemeev SV, Chulkov EV. Ab initio study of 2DEG at the surface of topological insulator Bi₂Te₃. *JETP Letters.* 2012; 95(4): 213–218
15. Ereemeev SV, Koroteev YuM, Chulkov EV. Effect of the atomic composition of the surface on the electron surface states in topological insulators A₂^VB^{VI}₃. *JETP Letters.* 2010; 91(8): 387–391
16. Ereemeev SV, Landolt G, Men'shchikova TV, Slomski V, Koroteev YM, Aliev ZS et al. Atom-specific spin mapping and buried topological states in a homologous series of topological insulators. *Nature Communications.* 2012; 3: 1638-1641
17. Sumalay R, Meyerheim HL, Ernst A, Mohseni K, Tusche C, Aliev ZS et al. Tuning the Dirac Point Position in Bi₂Se₃(0001) via Surface Carbon Doping. *Phys. Rev. Lett.* 2014; 113: 116802-116802-5.
18. Politano A, Caputo M, Nappini S, Bondino F, Aliev ZS, Babanly MB, Chulkov EV. Exploring the surface chemical reactivity of single crystals of binary and ternary bismuth chalcogenides. *J. Phys. Chem. C.* 2014; 118: 21517-21522.
19. Nechaev A, Aguilera I, De Renzi V, di Bona A, Rizzini AL, Mio AM et al. Quasiparticle spectrum and plasmonic excitations in the topological insulator Sb₂Te₃. *Phys. Rev. B.* 2015; 91: 245123-8
20. Ereemeev SV, Koroteev YuM, Chulkov EV. On possible deep subsurface states in topological insulators: The PbBi₄Te₇ system. *JETP Letters.* 2010; 92(3): 161–165
21. Men'shikova TV, Ereemeev SV, Koroteev YuM, Kuznetsov VM, Chulkov EV. Ternary compounds based on binary topological insulators as an efficient way for modifying the Dirac cone. *JETP Letters.* 2011; 93(1): 15–20

- 313 22. Okamoto K, Kuroda K, Miyahara H, Miyamoto K, Okuda T, Aliev ZS. et al. Observation
314 of a Highly Spin Polarized Topological Surface State in GeBi_2Te_4 . *Phys. Rev.* 2012; B
315 86: 195304
- 316 23. Okuda T, Maegawa T, Ye M, Shirai K, Warashina T, Miyamoto K et al. Experimental
317 Evidence of Hidden Topological Surface States in PbBi_4Te_7 . *Phys. Rev. Lett.* 2013; 111:
318 206803
- 319 24. Niesner D, Otto S, Hermann V, Fauster Th, Men'shchikova TV, Ereemeev SV et al. Bulk
320 and surface electron dynamics in a p-type topological insulator SnSb_2Te_4 . *Phys.Rev. B.*
321 2014; 89: 081404-081404-5
- 322 25. Ishizaka K, Bahramy MS, Murakawa H, Sakano M, Shimojima T, Sonobe T et al. Giant
323 Rashba-type spin splitting in bulk BiTeI . *Nature Mater.* 2011; 10: 521
- 324 26. Landolt G, Ereemeev SV, Aliyev ZS, Babanly MB, Amiraslanov IR. et al. Disentanglement
325 of surface and bulk Rashba spin splitting in noncentrosymmetric BiTeI . *Phys.Rev.Lett.*
326 2012; 109: 116403-116407
- 327 27. Isaeva A, Rasche B, Ruck M. Bismuth-based candidates for topological insulators:
328 Chemistry beyond Bi_2Te_3 . *Phys.St.Sol. RRL.* 2013; 7: 39–49.
- 329 28. Ereemeev SV, Nechaev IA, Chulkov EV. Giant Rashba-type spin splitting at polar
330 surfaces of BiTeI . *JETP Letters.* 2012; 96(7): 437-444
- 331 29. Ereemeev SV, Rusinov IP, Nechaev IA and Chulkov EV. Rashba split surface states in
332 BiTeBr . *New J. Phys.* 2013; 15: 075015
- 333 30. Chen YL, Kanou M, Liu ZK, Zhang HJ, Sobota JA, Leuenberger D. Discovery of a
334 single topological Dirac fermion in the strong inversion asymmetric compound
335 BiTeCl . *Nature Physics.* 2013; 9: 704-708
- 336 31. Ereemeev SV, Koroteev YuM, Chulkov EV. Ternary thallium-based semimetal chalcogenides
337 TI-V-VI_2 as a new class of three-dimensional topological insulators. *JETP*
338 *Letters.* 2010; 91(11): 594-597
- 339 32. Kuroda K, Ye M, Kimura A, Ereemeev SV, Krasovskii EE, Chulkov EV et al.
340 Experimental realization of a three-dimensional topological insulator phase in ternary
341 chalcogenide TlBiSe_2 . *Phys. Rev. Lett.* 2010; 105: 146801-4
- 342 33. Kuroda K, Ye M, Schwier EF, Nurmamat M, Shirai K, Nakatake M et al. Experimental
343 verification of the surface termination in the topological insulator TlBiSe_2 using core-
344 level photoelectron spectroscopy and scanning tunneling microscop. *Phys. Rev.B.*
345 2013; 88: 245308
- 346 34. Pielmeier F, Landolt G, Slomski B, Mu S, Berwanger J, Eich A et al. Response of the
347 topological surface state to surface disorder in TlBiSe_2 . *New J.Phys.* 2015; 17: 023067-
348 8
- 349 35. Garate I, Franz M. Inverse spin-galvanic effect in the interface between a topological
350 insulator and a ferromagnet. *Phys. Rev. Lett.* 2010; 104:146802
- 351 36. Men'shov VN, Tugushev VV, Chulkov EV. Bound states induced by a ferromagnetic
352 delta-layer inserted into a three-dimensional topological insulator. *JETP.* 2012; 96(7):
353 445-451
- 354 37. Kim H-Jung, Kim K-S, Wang J.-F., Kulbachinskii VA, Ogawa K, Sasaki M et al.
355 Topological phase transitions driven by magnetic phase transitions in $\text{Fe}_x\text{Bi}_2\text{Te}_3$
356 ($0 \leq x \leq 0.1$) single crystals. *Phys. Rev. Lett.* 2013; 110: 136601
- 357 38. Yokoyama T. Current-induced magnetization reversal on the surface of a topological
358 insulator. *Phys. Rev.B.* 2011; 84: 113407
- 359 39. Mahfouzi F, Nagaosa N, Nikolic BK. Spin-orbit coupling induced spin-transfer torque
360 and current polarization in topological-insulator/ferromagnet vertical heterostructures.
361 *Phys. Rev. Lett.* 2012. 109: 166602
- 362 40. Mellnik R, Lee JS, Richardella A, Grab JL, Mintun PJ, Fischer MH et al. Spin-transfer
363 torque generated by a topological insulator. *Nature.* 2014; 511: 449–451
- 364 41. Gottstein G. *Physical Foundations of Materials Science.* Springer-Verlag Berlin
365 Heidelberg; 2004.

- 366 42. Abrikosov NX. Semiconductor Chalkogenides and Alloys Based on Them, Nauka.
367 Moscow; 1975. In Russian
- 368 43. Binary alloy phase diagrams, Ed. T.B. Massalski, second edition (3 volume). ASM
369 International, Materials Park, Ohio; 1990,
- 370 44. Petzow G, Effenberg G.: Ternary alloys. A comprehensive compendium of evaluated
371 constitutional data and phase diagrams. ASM International. USA; 1992
- 372 45. Emsley J. The Elements, third ed., Clarendon Press; 1998.
- 373 46. Babanly MB, Aliev ZS, Amiraslanov IR. Physico-chemical aspects of the development
374 of topological insulators - a new class of functional materials. Az. Chem. J. 2015; 3: 6-
375 44. In Russian
- 376 47. Laudise R. A. Growth of Single Crystals New York: Prentice Hall; 1970.
- 377 48. Mullin JV. Single Crystal Growth I: Melt Growth. Electronic Materials. Springer.
378 Plenum Press, New York; 1991
- 379 49. Rao CNP. Gopalakrishnan J. New Directions in Solid State Chemistry. Cambridge
380 University Press; 2nd edition; 1997.
- 381 50. Gaumann A, Bohac P. Das Thermische Zustands Diagram $\text{Sb}_2\text{Se}_3/\text{Ti}_2\text{Se}$. J. Less.
382 Common. Metals. 1973. 31(2):314-316
- 383 51. Botgros IV, Zbigli KR, Stanchu AV, Stepanov GI, Cheban AG, Chumak GD. The
384 $(\text{Ti}_2\text{Se})_{3x}-(\text{Sb}_2\text{Se})_{1-x}$ system. Inorg.Mater. 1975; 11(11): 1953-1956
- 385 52. Gotko NP, Kirilenko VV, Churbanov VV, Schelokov RN. The Ti-Sb-Se system. Inorg.
386 Mater. 1986; 22(9):1438-1447
- 387 53. Babanly MB, Dzhafarov YI, Kuliev AA. $\text{Ti}_2\text{Se}-\text{Sb}_2\text{Se}_3$ and $\text{TiSe}-\text{TiSbSe}_2$ (Ti_9SbSe_6)
388 systems. Russ.J.Inorg.Chem. 1998; 43(5): 779-781
- 389 54. Babanly MB, Dzhafarov YI, Kuliev AA. Phase equilibria and thermodynamic properties
390 of the Ti-Sb-Se system. Russ.J.Phys.Chem. 1987; 61(10):2599-2604.
- 391 55. Mucha I. Reinvestigation of phase equilibria in the thallium(I) selenide- antimony (III)
392 selenide system. Thermochim. Acta. 2013; 563: 6-11
- 393 56. Dzhafarov YI, Babanly MB, Kuliev AA. $\text{Ti}_2\text{Se}-\text{Sb}$, $\text{Ti}_9\text{SbSe}_6-\text{Sb}$, $\text{TiSe}-\text{Sb}$ and $\text{TiSbSe}_2-\text{Sb}$
394 systems // Russ.J.Inorg.Chem. 1998; 43(4): 619-621
- 395 57. Dzhafarov YI, Babanly MB, Kuliev AA. The Ti-Sb-Se system. Russ.J.Inorg.Chem.
396 1998; 43(8): 1278-1284
- 397 58. Zbigli KR, Raevskii SD. Phase diagram of the $\text{Bi}_2\text{Se}_3-\text{Ti}_2\text{Se}$ system. Inorg. Mater. 1984:
398 20(2): 211-214.
- 399 59. Babanly MB, Zamani IS, Akhmadyar A, Kuliev AA. Phase equilibria and thermodynamic
400 properties of the $\text{Ti}_2\text{Se}-\text{Bi}_2\text{Se}_3-\text{Se}$ system. Russ.J.Inorg.Chem. 1990; 35(5): 1285-1289
- 401 60. Sztuba Z, Mucha I, Gawel W. Phase equilibria in the quasi-binary thallium(I) selenide-
402 bismuth(III) selenide system. Polish J.Chem. 2004; 78: 789-794
- 403 61. Babanly MB, Popovkin BA., Zamani IS, Guseynova RR. Phase equilibria in the Ti-Bi-
404 Se system. Russ.J.Inorg.Chem. 2003; 48(2): 2091-2213
- 405 62. Botgros IV, Zbigli KR, Stanchu AV, Stepanov GI, Chumak GD. Section $\text{Ti}_2\text{Te}-\text{Sb}_2\text{Te}_3$ of
406 the Ti-Sb-Te system. Inorg. Mater. 1977; 13: 1202-1206.
- 407 63. Babanly MB, Akhmadyar A, Kuliev AA. Thermodynamic properties of intermediate
408 phases in the Ti-Sb(Bi)-Te systems. Russ.J.Phys.Chem. 1985; 59(3): 676-678
- 409 64. Akhmadyar A, Babanly MB, Kuliev AA. Interaction of thallium and stibiumtellurides.
410 Az.Chem.J. 1984; 3: 96-99. In Russian
- 411 65. Babanly MB, Akhmadyar A, Kuliev AA. The Ti-Sb-Te system. Russ.J.Inorg.Chem. 1985;
412 30 (4): 1051-1059
- 413 66. Berg LG, Abdulmanov AG. Quasibinary system $\text{Bi}_2\text{Te}_3-\text{Ti}_9\text{BiTe}_6$. Inorg. Mater 1970;
414 6(12): 2192-2193
- 415 67. Babanly MB, Akhmadyar A, Kuliev AA. The $\text{Ti}_2\text{Te}-\text{Bi}_2\text{Te}_3-\text{Te}$ system. Russ. J. Inorg.
416 Chem. 1985; 30(9): 2356-2361
- 417 68. Pradel A, Tedenac J-C, Brun G, Maurin M. Mise au point dans le ternaire Ti-Bi-Te.
418 Existence de deux phases nonstoechiometriques de type TiBiTe_2 . J. Sol. State Chem.

- 1982; 45 (1): 99-111
69. Gawel W, Zaleska E, Terpilowski J. Phase diagram for the $Tl_2Te-Bi_2Te_3$ system // J. Therm. Anal. 1989. v.35. P.59-68
70. Jafarov YI, Imamaliyeva SZ, Babaev AK, Babanly MB. Thermodynamic investigation of the $Tl-Bi-Te$ system by EMF method. Az.Chem.J. 2013; 4: 75-79. In Russian.
71. Babanly MB, Yusibov YuA, and Abishev VT. The EMF method in the thermodynamics of compound semiconductors. BGU. Baku; 1992. In Russian.
72. Babanly MB, Yusibov YI. Electrochemical methods in thermodynamics of inorganic systems. Baku; 2011. In Russian.
73. Babanly MB, Veysova SM, Guseinov ZA, Jafarov YI. The $Tl_2Se-Sb_2Se_3-Bi_2Se_3$ system Russ.J.Inorg.Chem. 2002; 47(6): 1020-1025
74. Veysova SM, Guseinov ZA, Guseinov FN, Babanly MB. Phase equilibria and thermodynamic properties of the $Tl_2Te-Sb_2Te_3-Bi_2Te_3$ system. News of Baku Univ. Nat. Sci. Ser. 2004; 3: 10-20. In Russian.
75. Jafarov YI, Mirzoeva AM, Babanly MB. Reciprocal system $3Tl_2S+Sb_2Se_3 \leftrightarrow 3Tl_2Se+Sb_2S_3$. Russ.J.Inorg.Chem. 2008; 53(1):146-152
76. Jafarov YI, Mirzoeva AM, Babanly MB. Reciprocal system $3Tl_2S+Bi_2Se_3 \leftrightarrow 3Tl_2S+Bi_2Se_3$. Russ.J.Inorg.Chem. 2006; 51(5): 871-875
77. Jafarov YI. The system $Tl_2S-Tl_2Te-Tl_9SbTe_6$ and comparative analysis of the phase diagrams of related systems. Adv.Cur. Nat. Sci. 2013; 1:88-91. In Russian.
78. Jafarov YI, Babanly MB, Amiraslanov IR, Qasimov VA, Shevelkov AV, Aliev ZS. Study of the $3Tl_2S+Sb_2Te_3 \leftrightarrow 3Tl_2Te+Sb_2S_3$ reciprocal system. J. Alloy. Compd. 2014; 551: 512-520
79. Jafarov YI. New variable compositions phases in reciprocal system $3Tl_2Se+Sb_2Te_3 \leftrightarrow 3Tl_2Te+Sb_2Se_3$. Az.Chem.J.2012; 4: 111-116. In Russian.
80. Jafarov YI, Shevelkov AV, Babanly MB, Aliev ZS. Experimental investigation of the $3Tl_2Se+Sb_2Te_3 \leftrightarrow 3Tl_2Te+Sb_2Se_3$ phase diagram. J.Alloy.Comp.2013; 555: 184-192
81. Jafarov YI, Rzaeva NA, Babanly MB. Phase equilibria in the $Tl_2S-Tl_2Te-Tl_9BiTe_6-TiBiS_2$ system. Inorg. Mater. 2008; 44(11): 1183-1186
82. Jafarov YI. The system $TiBiS_2(Bi_2Te_2S)-TiBiTe_2$. J.Qafqaz Univ.- Phys. 2014; 2(1):92-95
83. Jafarov YI, Imamaliyeva SZ, Zlomanov VP, Babanly MB. Phase equilibria in the reciprocal system $3Tl_2S+Bi_2Te_3 \leftrightarrow 3Tl_2Te+Bi_2S_3$. Inorg. Mater. 2014; 50(6): 551-558
84. Babanly MB, Veysova SM, Guseynov ZA, Yusibov YA. Reciprocal system $3Tl_2Se+Bi_2Te \leftrightarrow 3Tl_2Te+Bi_2Se_3$. Russ.J.Inorg.Chem. 2003; 48(9): 2562-1568.
85. Man LI and Semiletov SA. Electronographic studing the $TiBiX_2$ ($X=S, Se, Te$). Kristallografia. 1962; 7: 884.
86. Hockings EF and White JG. The crystal structures of $TiSbTe_2$ and $TiBiTe_2$. Acta Crystallogr. 1961; 14: 328.
87. Teske CL and Bensch W. $TiBiTe_2$. Acta Crystallogr. Sect. E. 2006; 62: i163-i165.
88. Cava RG, Ji H, Fuccillo MK, Gibson QD, Hor YS. Crystal structure and chemistry of topological insulators. J. Mater. Chem. C. 2013; 1: 3176