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PHYSICOCHEMICAL ASPECTS OF TERNARY AND COMPLEX PHASES DEVELOPMENT BASED ON THALLIUM CHALCOHALIDES

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The results of physical and chemical investigation of some ternary and more complex systems which are of interest in terms of obtaining thallic chalcohalides and new multicomponent phases on their basis have been systematized and analyzed in the review paper. This class of inorganic substances is of scientific and practical interest as promising functional materials with thermoelectric, optical, magnetic, sensor and detector properties. The literature data on crystal structure, thermodynamic and some physico-chemical properties of thallium chalcohalides and intermediate phases on their basis have been investigated.

Keywords: *thallium chalcohalides, functional materials, phase diagram, solid solutions, thermodynamic properties, crystal structure.*

1. Introduction

Chalcogenides and chalcohalides of heavy metals, including *5p* and *6p* elements, are in the cenre of attention of world scientists since the middle of the last century due to their interesting chemical bonding characteristics and fascinating physical properties [1-5]. Many of them are applied or considered perspective for application in various fields of electronics and high technologies.

The discovery of research achievements in nanomaterials over the past two-three decades [6,7] and the discovery of graphene [8] and topological insulators (TI) [9-11] have given a powerful impetus to the development of electronics and other high technologies. The discovery of graphene stimulated the search for other graphene-like two-dimensional materials, among which 2D transition metal chalcogenides, due to their unique physical properties, proved extremely promising for use in new generation optoelectronic devices [12-16].

The most important applications of TI materials are new spin-off devices and permanent transistors for quantum computers, based on the quantum spin Hall effect [9-11, 17] and the anomalous quantum Hall effect [18]. These materials are also prospective for application in superior magnetoelectronics, optoelectronics, security systems, and so on [19-21]. Currently the most widely studied substances like TI are Bi_2Se_3, Bi_2Te_3, Sb_2Te_3 compounds and phases based on them [9-11, 22, 23]. However, recent studies have shown that a number of tetradimide-based compounds formed in A^{IV}-B^{V}-Te systems also posess interesting TI properties [11, 24-27].

Heavy metal chalcogenides play an important role among the new photoelectric, thermoelectric materials and other energy-transducers generated for the use of alternative and renewable energy sources [28-31]. These materials are also used to create highly sensitive sensors and detectors for the implementation of various complex technological processes, as well as, for monitoring environmental safety on Earth in in the atmosphere [7, 32].

Chalcohalogenides of heavy metals, including 5p- and 6p-elements occupy a special place among the above mentioned promising materials for application in many other areas [3, 33-43]. For example, ferroelectric semiconductors of type B^{V}XHal (B^{V}-Sb, Bi, X-S, Se, Te, Hal, Cl, Br, I) possess precious photoelectric, magnetic, electrooptic, pyroelectric, pyro-optic and other properties and consiredered to be promising for application as nuclear, γ- and infrared beam detectors, light modulators, gas sensors, photon crystals, memory elements, etc.[33-35].

It is expected that the Rashba effect, which provides spin manipulation through the electric fields of these materials, will be used in devices proposed as a spin field and spin Hall transistors [36-40]. The most recent materials proposed in this direction are, for example, spin-orbit coupling, ferroelectric semiconductors controlled by electric polarization [41-43].

Over the last decade, the phase equilibrium, thermodynamic properties of B^V-X-I systems have been studied extensively, primary crystallization areas and fundamental thermodynamic functions of intermediate phases, including B^VXI compounds, have been determined [44-48].

Numerous studies have shown that ternary chalcogenides and chalcohalogenides of 6p (Tl, Pb, Bi) and 5p (Sn, Sb) elements have an anomalous low thermal conductivity and high thermoelectric efficiency [29-31].

According to recent studies, thallium chalcogenides and ternary chalcohalide hybrids (Tl_6SeI_4,Tl_6SI_4) have potential applications, such as radiation detectors, and form a new class of inorganic semiconductor detector materials [49-57]. These compounds and phases on their basis are far more promising than CZT ($Cd_{0.9}Zn_{0.1}Te$) of industrial importance - the most sensitive detector material for functional indications, and are one of the most promising materials for new generation electronic devices. Even though the talium compounds are toxic, compounds and intermediate phases containing thallium have an important place among such materials that have unusual electronic properties. It has been established that three-dimensional seleno- and thioiodides of thallium have three-dimensional structure (3D) and therefore possess better internal electronic and mechanical properties, demonstrating both high hole and electron conductivity compared to linear (1D) and layered (2D) compounds [49-52].

$Tl_6S(Se)I_4$ monocrystals were studied, their electron structure, dielectric, optical properties and structure defects examined [53-54]. It has been established that these ternary compounds have higher mechanical strength and optimal band gap value for radiation detectors compared to TlI and $Tl_2S(Se)$ binary compounds that form them.

Note that the establishment of scientific basis for the directional search and synthesis of new multicomponent inorganic materials with a combination of physical and physico-chemical properties requires a complex analysis of the corresponding systems, their phase diagrams, and the determination of the fundamental thermodynamic functions of the intermediate phases [58, 59]. From this point of view, it is of particular interest to have a complex physical-chemical study of complex systems known to be formed of solid analogues or solid solutions based on known binary and triple compounds with valuable application properties. Therefore, a physicochemical investigation of complex systems composed of structure analogs of known binary and ternary compounds with valuable application properties or solid solutions based on them is of particular interest.

The review article summarized and comparatively analyzed the literature data and experimental results obtained by the authors on the ternary Tl-X-Hal systems, Tl_2Te-TlHal-TlHal$^/$ and Tl_5Te_3-Tl_9BiTe_6-Tl_5Te_2Hal concentration ranges of the Tl-X-X$^/$-Hal və Tl-X-Hal-Hal$^/$ (X,X$^/$ -S,Se,Te; Hal,Hal$^/$ -Cl,Br,I) quaternary systems, and on the phase equilibria, thermodynamic, crystallographic and some physicochemical properties of the complex thallium chalcohalogenide systems.

2. Phase equilibria in the Tl-X-Hal (X-S, Se, Te, Hal -Cl, Br, I) systems and some physico-chemical properties of intermediate phases

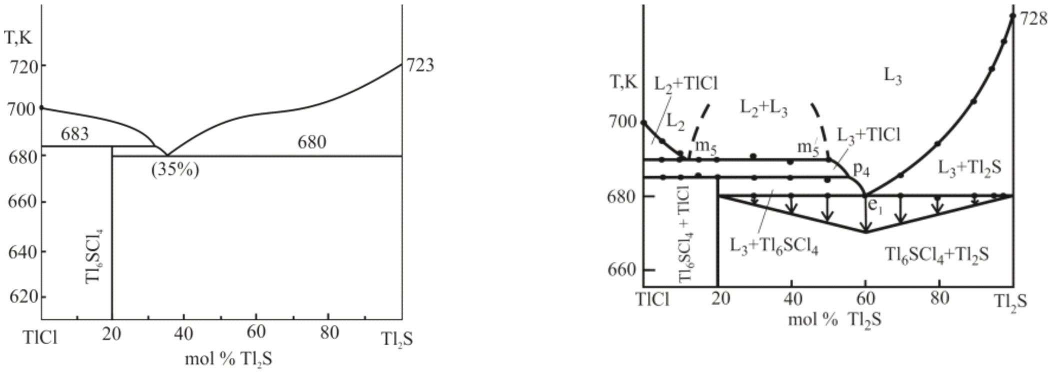
Initial researches on Tl-X-Hal (X-S, Se, Te, Hal -Cl, Br, I) systems began in the 1980-s with the stydy of Tl_2X-TlHal and TlX-TlHal quasibinary sections.

2.1. Phase equilibria in the Tl – S – Cl (Br,I) systems

Tl-S-Cl system. TlCl-Tl_2S quasi-binary section of this system is of peritectic type [60, 61] and forms a congruently melted Tl_6SCl_4 ternary compound at 683 K (Fig. 1, a). In [62], the system was re-visited, formation of the Tl_6SCl_4 peritectic ternary compound was confirmed and coordinates of the peritectic and eutectic equilibriums were found to be essentially different from the results of the [60.61] (Fig.1, b). In contrast to [60,61], existence of the immiscibility area (~13-50 mol% Tl_2S) of two liquid phases has been established [62].

The system was studied at the Tl-TlCl-S concentration range by means of DTA, X-ray and SEM analysis, as well as through the measurement of microhardness and EMF. A series of polythermal and isothermal sections, liquidus sufrace projection of its phase diagram was constructed [62-64].

It found that TlCl-S system is also a quasibinary, forming a phase diagram with a monotectic and degenerated eutectic equilibrium near the sulfur [63].

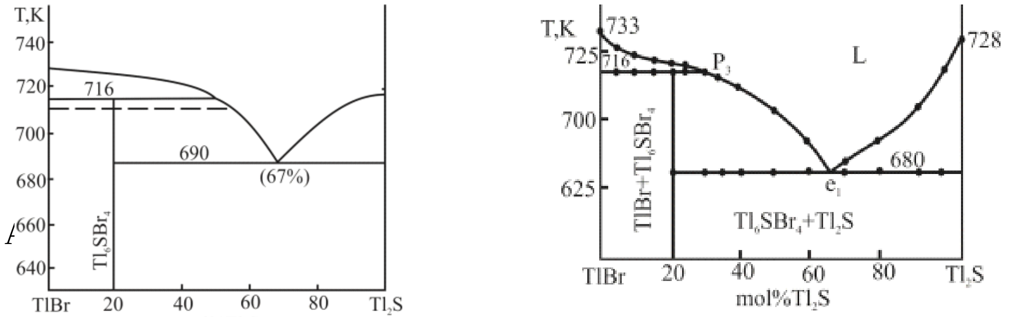


a) b)

Fig 1. Phase diagram of the system TlCl-Tl_2S: a) - [61], b) - [63]

Tl-S-Br system. TlBr-Tl_2S and TlBr-S sections of this ternary system are quasi-binary [65,66]. According to [60], TlBr-Tl_2S system is characterised by formation of incongruently melting ternary Tl_6SBr_4 compound at 716K (Fig.2,a). The phase equilibrium in the system was re-examined; the formation of the above mentioned ternary compound proved, and coordinates of nonvariant equilibria specified (Fig. 2,b) [66].

TlBr-S system is of monotectic and degenerated eutectic type. Tl – S – Br ternary system was investigated at the Tl-TlBr-S concentration range, some isopleth sections and the projection of the liquidus surface of its phase diagram were constructed, types and coordinates of non- and monovariant equilibria determined [65,66].



a) b)

Fig.2. Phase diagram of the system TlBr-Tl_2S: a) - [61], b) - [67]

Tl – S – I system. TlI-Tl_2S quasi-binary section is characterized by formation of ternary Tl_6SI_4 compound melting congruently at 713K, and a phase of the Tl_3SI composition that is stable at 640-670K temperature intervale [61]. According to the results of [60], Tl_6SI_4 melts congruently at 710K and has a ~4 mol % (according to [67,68] ~2 mol %) homogeneity area [69] report that, Tl_6SI_4 melts congruently at 710K, Tl_3SI – incongruently at 673K by peritectic reaction. The latter decomposes at 653K according to solidphase reaction into Tl_2S and Tl_6SI_4 compounds.

The full description of phase equilibria of the Tl-S-I ternary system is given in the Fig.3 [65,69,70]. Three polythermic sections (TlI-Tl_2S, TlI-S və Tl_6SI_4-Tl) of this system are quasi-binary. TlI-S and Tl_6SI_4–Tl systems are characterized by monotectic and eutectic equilibriums.

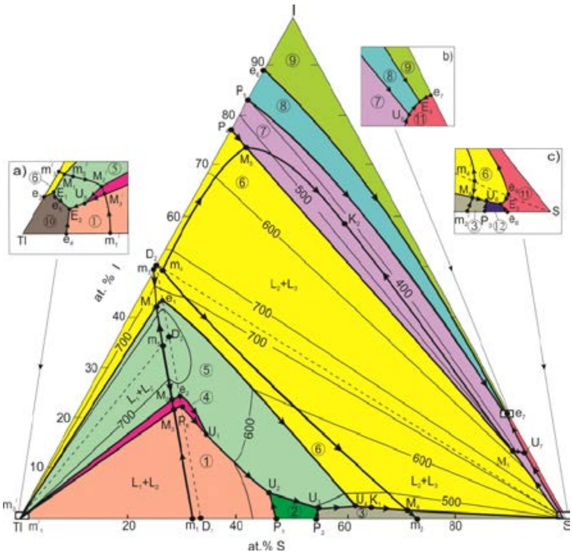
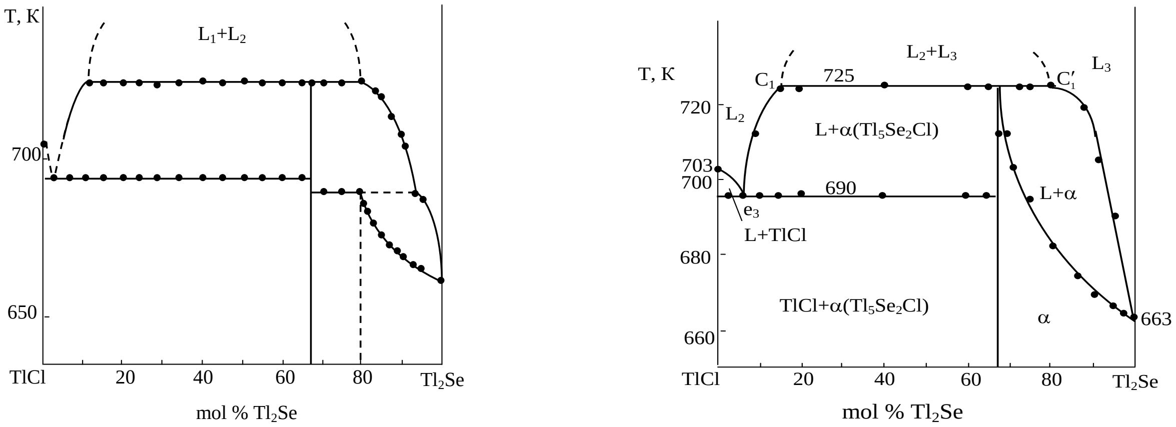


Fig. 3. The projection of the liquidus surface of the system Tl-TlI-S. Primary crystallization areas: 1–Tl_2S, 2–Tl_4S_3, 3–TlS, 4–Tl_3SI, 5–Tl_6SI_4 (γ), 6–$(TlI)_{II}$, 7–Tl_2I_3, 8–TlI_3, 9- I_2, 10–Tl, 11–S and 12–Tl_2S_5

There are 2 immiscibility areas in the system Tl-S-I. Monovariant eutectic and peritectic equilibrium curves are transformed into nonvariant monotectic equilibria while intersecting this immiscibility regions (Fig.3 - $M_1M_1^{/}$, $M_2M_2^{/}$, $M_3M_3^{/}$, $M_4M_4^{/}$, $M_5M_5^{/}$ conjugate pairs).

2.2. Phase equilibria in the Tl – Se – Cl (Br,I) systems

Tl – Se – Cl system. A ternary compound Tl_5Se_2Cl melting by sintectic reaction at 725K is formed in the first version of the Tl_2Se-TlCl phase diagram [71] (Fig.4a). This compound is in eutectic equilibrium with TlCl, and in peritectic equilibrim with Tl_2Se. The homogeneity area of Tl_2Se at the peritectic reaction temperature is ~20 mol%. The T-x diagram of this system constructed by [72] (Fig. 4,b) is consistent at 0-66.7 mol% Tl_2Se composition intervale with results of [71]. However, results obtained by [72,73] at the Tl_5Se_2Cl-Tl_2Se composition range differs qualitatively from those given in [71] and is characterized by formation of continious solid solutions. Note that this agrees with the fact that the primary constituents of the sub-system Tl_5Se_2Cl-Tl_2Se are iso-structural (see section 3).



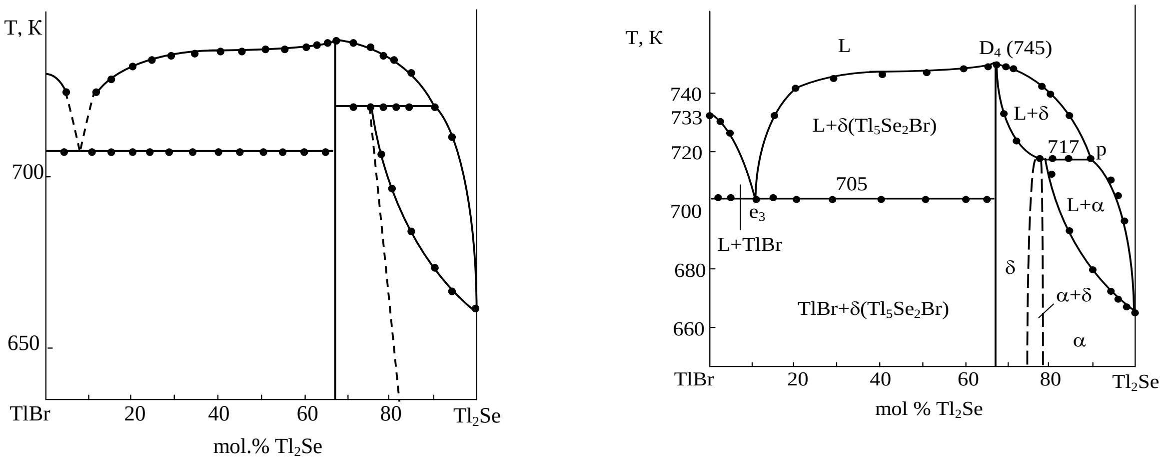
a) b)

Fig. 4. Phase diagram of the system Tl_2Se-TlCl: a) –[72], b) – [73]

TlSe-TlCl section is also quasi-binary and forms a phase diagram having monotectic and eutectic equilibria [60]. The Tl-S-Cl ternary system was studied in detail at the Tl-TlCl-Se concentartion interval, and some izopleth sections, izothermal section at 400K , as well as the projection of the liquidus surface of its were constructed [72-76].

Tl – Se – Br system. TlBr-Tl_2Se system forms a congruently melting ternary compound Tl_5Se_2Br [71] (Fig.5a). It is stoichiometric to be in eutectic equilibrium with TlBr (~10 mol%Tl_2Se, 705K), and in peritectic equilibrium with Tl_2Se (~90 mol %Tl_2Se, 720K). There is a wide solid solution area (75-100 mol% Tl_2Se, 720K) based on Tl_2Se [71]. New phase diagram [73,77] of the system TlBr-Tl_2Se coincides with the results of [71] at the TlBr-Tl_5Se_2Br composition interval, whereas it differs considerably from it at the Tl_5Se_2Br-Tl_2Se interval (Fig.5b). According to [71], Tl_5Se_2Br forms a large (66.7-75 mole% Tl_2Se) solid solution area.The results of Ref. [71] agree with the results of Ref. [78-80] that Tl_5Se_2Br is of variable composition.

Experimental results in the Tl-TlBr-Se concentration range were summarized, some polythermal and isotermal sections, liquidus surface projection constructed in Ref. [77].



a) b)

Fig.5. Phase diagram of the system Tl_2Se-TlBr: a) – [72], b) – [78]

Tl – Se –I system. The phase equilibria in the Tl–Se–I ternary system was investigated in a whole concentartion range [60, 65, 71, 81-86]. Both ternary compounds - Tl_5Se_2I and Tl_6SeI_4 detected in the Tl-Se-I system are formed on the TlI–Tl_2Se section [60, 71, 83-84]. Tl_5Se_2I melts congruently at 720K, Tl_6SeI_4 melts by peritectic decomposition at 705K [71]. Tl_5Se_2I has a wide hogeneity region and is in peritectic equilibrium with Tl_2Se. However, according to the results of [60], both compounds are non-stoichiometric phases which melt congruently.

A re-study of the TlI-Tl_2Se system [83,84] confirmed the existence of congruently melting ternary compounds Tl_5Se_2I (720K) and Tl_6SeI_4 (705K).

TlSe–TlI [60], TlSe–Tl_5Se_2I and TlSe–Tl_6SeI_4 [84,85] polythermal sections of the system Tl–Se–I are quasi-binary and form eutectic phase diagram. TlI-Se [86], Tl_5Se_2I-Tl [84] vә Tl_6SeI_4-Tl [84] polythermal sections are also quasi-binary and characterized by monontectic and degenerated eutectic equilibriums.

The projection of the liquidus surface of the system Tl-Se-I is given by the Ref. [65,84]. It consists of 10 primary crystallization areas (Fig.6). Liquidus surfaces of the elemenetal Tl and Se are degenerated on the relevant vertices of a concentration triangle. The largest area of crystallization belongs to the high temperature modification of thallium monoiodide - $(TlI)_{II}$. This compound involves most non- and monovariant equilibriums in the Tl-Se-I system.

Tl-Se-I system is divided into 8 sub-systems by 7 quasi-binary sections (Fig.6, dashed lines). 3 of those sub-systems (Tl-TlI-Tl_6SeI_4, Tl-Tl_6SeI_4-Tl_5Se_2I, TlI-TlSe-Se) are characterized by nonvariant monotectic and eutectic equilibria, two of them (TlI-Tl_6SeI_4-TlSe, Tl_6SeI_4-Tl_5Se_2I-TlSe) are of eutectic type, one - Tl_2Se-Tl_5Se_2I-TlSe is of transition type, and one - Tl-Tl_2Se-Tl_5Se_2I is of monotectic and transition types. The latter system - TlI-Se-I covers half of the concentration triangle and reflects a series of non- and monovariant equilibria. The hogeneity areas and dissociation in the liquid state of the Tl_5Se_2Hal and $Tl_6S(Se)I_4$ compounds are comprehensively studied [61,67,68,78-80].

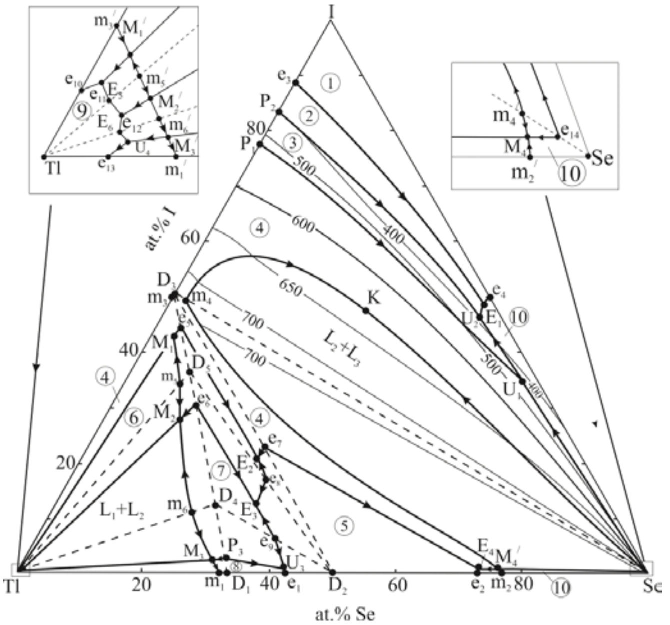


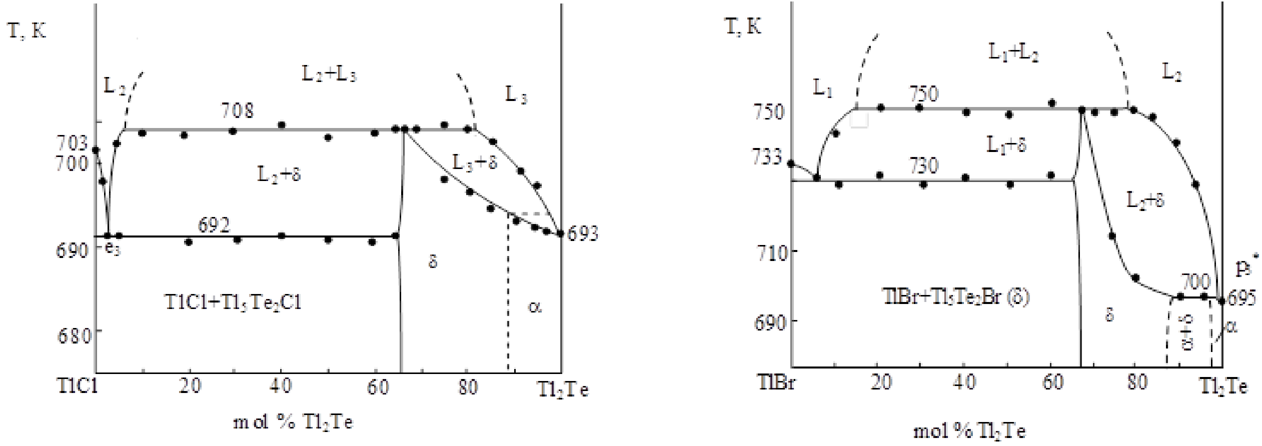
Fig.6. The projection of the liquidus surface of the system Tl-Se-I. Primary crystallization areas: 1–I_2, 2–TlI_3, 3–Tl_2I_3, 4–$(TlI)_{II}$, 5–TlSe, 6 –Tl_6SeI_4, 7–Tl_5Se_2I (δ-phase), 8–Tl_2Se (α-phase), 9–Tl, 10–Se.

2.3. Phase equilibria in the Tl – Te – Cl (Br,I) systems

Tl – Te – Cl system. Phase equilibria in this system were studied by TlCl-Te(TlTe,Tl_2Te_3), Tl_5Te_2Cl-Tl(TlTe,Tl_2Te_3,Tl_5Te_3) polythermal sections [73,76,87-89]. The further study of phase equilibria in the Tl-TlCl-Te composition area was carried out by [90-92], a number of polythermal sections, the projection of a liquidus surface of the system constructed, types and coordinates of non- and monovariant equilibriums determined.

$TlCl$-Tl_2Te quasi-binary section is characterized by formation of ternary Tl_5Te_2Cl that melts incongruently by syntectic reaction at 708 K [90,92]. The aliquation area at this temperature ranges between ~7-85 mol% Tl_2Te concentration region. Tl_5Te_2Cl is in eutectic equilibrium with TlCl, whereas it is a solid solution area with Tl_2Te (Fig. 7,a).

The main feature of the system Tl-TlCl-Te is the existence of a wide immisciblity areas on the basis of 3 different liquid phases. These aliquaition fields cover more than 90% of the Tl-TlCl-Te concetration triangle. There is a wide triple immiscibility region which is surrounded by corresponding double immiscbility areas [92].



a) b)

Fig. 7. Phase diagram of the systems $TlCl$-Tl_2Te (a) [94] and $TlBr$-Tl_2Te (b) [97]

Tl – Te – Br system. This system was studied in the Tl-TlBr-Te composition area [87, 89, 91, 93-95]. It revealed that the only quasi-binary section of this system - $TlBr$-Tl_2Te forms a phase diagram with syntectic, eutectic and peritectic equilibriums. Tl_5Te_2Br melts by syntectic reaction at 750K. Its homogeneity area occupies 66.7-87 mol% Tl_2Te concentration interval [91,95] (Fig. 7,b).

TlBr-Te system is quasi-binary, whereas $TlBr$-$TlTe(Tl_2Te_3)$, Tl_5Te_2Br-$TlTe$, Tl_5Te_2Br-Tl_5Te_3 isopleth sections are stable in subsolidus. The latter forms a continuous series of solid solutions.

The projection of the liquidus surface consists of 5 fields which agrees with the primary crystallization of the TlBr, δ-phase, TlTe, Tl_2Te_3 and elemental Te [95]. Formation of the triple immiscibility area in the system is due to the presence of extensive double immiscibility areas on all sides of the Tl-TlBr-Tl_2Te subsystem. The triple immiscibility area is chracterized by the nonvariant syntectic $L_1+L_2+L_3 \rightarrow \delta$ reaction.

In Ref. [96-102] ternary compounds $Tl_2TeBr(I)_6$ were detected, their homogeneity areas defined and some properties of their moncrystals examined.

Tl – Te – I system was investigated in a whole concentration interval.

TlI-Tl_2Te quasi-binary section forms a ternary Tl_5Te_2I compound meltig at 775K by syntectic reaction [60]. Tl_5Te_2I is a phase of variable composition and has a ~10 mol % homogeneity region along the TlI-Tl_2Te system (Fig.8).

Tl_2TeI_6 compound melting congruently at 700K was detected on the TlI-TeI_4 quasi-binary section, its crystal structure and some physical properties were studied [97-102]. New option of the TlI-TeI_4 phase diagram [108] differs from the one described in Ref. [100] by melting temperature of Tl_2TeI_6 - 654K.

T-x-y digram of the Tl-Te-I system is given in [105-110]. It found that TlI-Te, TlI-Tl_2Te, TlI-TeI_4, Tl_2TeI_6-Te and Tl_2TeI_6-I polythermal sections are quasi-binary. The phase diagram of the TlI-Tl_2Te system has been specified by [98]. The results obtained are close to [60].

The solid-phase diagram of the Tl-Te-I system at 300K reflects 2 ternary compounds (Tl_5Te_2I; Tl_2TeI_6) and their equilibria with other phases. There is a wide homogeneity area based on Tl_5Te_2I, however Tl_2TeI_6 has almost a stoichiometric composition.

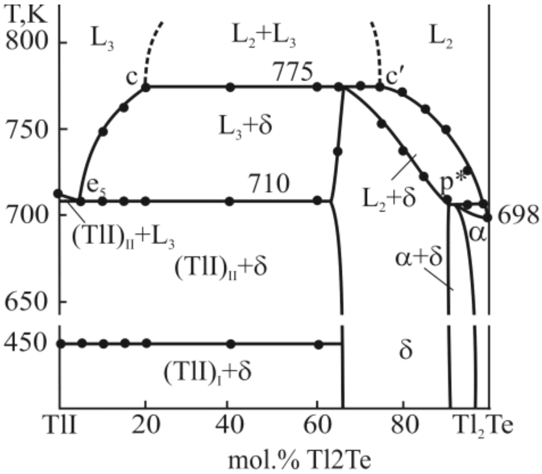


Fig. 8. Phase diagram of the system TlI–Tl_2Te

Projection of the liquidus surface consists of 11 primary crystallization areas (Fig.9) [108]. Liquidus surfaces of the elemental Tl and α-phase based on Tl_2Te are degenerated.

To sum up, let's look at characteristic features of phase equilibria in the Tl-X-Hal systems.

6 ternary compounds of the type Tl_5X_2Hal (in all Se and Te containing), 4 compounds of the type Tl_6XHal_4 (in all S containing systems) and Tl_2TeHal_6 compounds have been detected in the Tl-X-Hal systems. It revealed that all compounds, except for the latter ones, are formed on the TlHal-Tl_2X quasi-binary sections. Tl_5X_2Hal compounds decompose incongruently by syntectic reaction except for the Tl_5Se_2I and Tl_5Se_2Br that melt congruently. Tl_6XHal_4 compounds melt congruently (Tl_6SI_4 and Tl_6SeI_4) or by peritectic decomposition.

Tl_5X_2Hal compounds are phases of variable composition possessing a wide homogeneity area, whereas Tl_6XHal_4 and Tl_2TeHal_6 compounds are practically stoichiometric. Crystal structures of all three types of compounds are discussed in the next section.

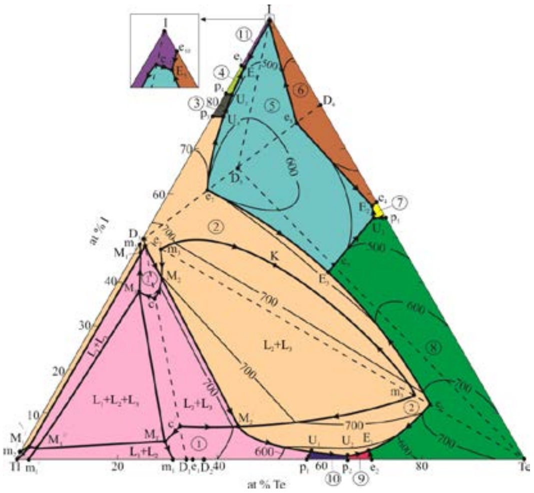


Fig.9. Liquidus surface projection of the system Tl-Te-I. Primary crystallization fields:

1- δ phase, 2- $(TlI)_{II}$, 3-Tl_2I_3, 4-TlI_3, 5-Tl_5Te_2I, 6-TeI_4, 7-TeI, 8-Te, 9-Tl_2Te_3, 10- TlTe, 11- I_2

The characteristic feature of the Tl-X-Hal systems is the existence of wide immiscibility areas in a liquid state. There are triple immiscibility areas together with double ones in the 6 systems out of the 9 Tl-X-Hal systems. The comparative analysis of the liquidus surfaces shows that the character phase of equilibria changes regularly in three directions of S→Se→Te and Cl→Br→I, which is due to changes in the nature of chemical bonding in these systems.

Criteria of aliquation was revealed in the T1-X-Hal ternary systems as a result of the comparative analysis of T-x diagrams of more than 50 quasi-binary and quasi-stable sections [109, 110]. It showed that there is an immiscibility area in the systems when the degree of ionisation (DOI) is more that 17, and the systems with DOI <16-17 don't demostrate aliquation.

To summarize, there is a rare case of practice in the Tl_5X_2Hal–Tl_2X and Tl_5Te_2Hal–Tl_5Te_3 sections of the Tl-X-Hal systems. Despite the presence of extensive immiscibility areas in liquid state, these systems are characterized by formation a wide or continuous solid solution areas in subsolidus.

3. Crystal structure and some physico-chemical properties of thallium chalcohalides

The literature data on the crystal structure and some physico-chemical properties of tallium chalco-halides are discussed in this section. As mentioned above (section 2), there are 3 types of ternary compounds in Tl-X-Hal systems: Tl_5X_2Hal, Tl_6XHal_4 and Tl_2TeHal_6. Crystal lattice types and parameters of those compounds are listed in the Table 1.

Tl_5X_2Hal compounds are crystallized in a tetragonal lattice of the Tl_5Te_3 type. The crystal structure of Tl_5Te_3 has been analyzed in a number of studies [111-114] following which this compound is crystallized in a tetragonal structure of the Cr_5B_3 type (Sp.gr. I4/*mcm*). In the unit cell there are 4 formula units (z = 4).

The main structural elements of the Tl_5Te_3 crystal lattice (Fig. 10) are tellurium octahedra in which tellurium atoms have two different positions: part (Te1) is located at two opposite vertices of octahedra along the *c* axis, and the other part (Te2) occupies the remaining positions.

Thallium atoms are also subdivided into 2 types according to their positions in the crystal lattice: one part of the cations - Tl (1) is located in equivalent positions with a multiplicity of 16, and another part - Tl (2) - in positions with a multiplicity of 4. Chemical composition of the unit cell is $Tl_{16}Tl_4Te_8Te_4$. Considering the electroneutrality condition, it can be assumed that in positions with a multiplicity of 4, the Tl^+ and Tl^{3+} cations alternate and the unit cell can be represented as $Tl_{16}[(Tl^{1+}_{0,5}B^{3+}_{0,5})Te_3]_4$. Linking to the vertices, the octahedra form a skeleton of the composition Tl_4Te_{12} or $(TlTe_3)_4$ (Fig. 10, a). Thallium prisms are formed around the octahedra, and antiprisms of thallium are formed around the anions at the vertices of the octahedra, which bind the octahedra along the *c* axis. Prisms and anti-prisms are alternated along the *c* axis. These structural elements create a structure of the Tl_5Te_3 type with the chemical composition of the cell $Tl_{16}(TlTe_3)_4$ (Fig. 10, b).

Due to the above mentioned features of the crystal lattice, Tl_5Te_3 forms a series of cation- and anion-substituted derivatives. Typical representatives of cation-substituted ternary analogues of Tl_5Te_3 are compounds of the types Tl_9BTe_6 (B-Sb, Bi, In, Au, rare earth elements) [115-119] and Tl_4ATe_3 (A-Sn, Pb, Cu, Mo, Nd) [115,118, 120-122].

Tl_4ATe_3 and $Tl_{16}[A^{2+}Te_3]_4$ compounds are formed when all the thallium atoms in the centers of the octahedra (Tl2) are replaced by the A^{2+} cations. Replacement of half of the Tl atoms located in the vacancies of octahedra (Tl2), with B^{3+} cations leads to the formation of Tl_9BTe_6 compounds [117].

The crystal structures of Tl_5X_2Hal compounds - anion-substituted derivatives of Tl_5Te_3 were studied in detail. According to the available data (Table 1), all these compounds, with an exception of Tl_5Se_2Cl (Sp.gr P4 / *ncc*), belong to the spatial group I4 / *mcm*. Se or Te atoms located at two opposite vertices of the octahedra are replaced by halogen atoms in the crystal lattices of these compounds.

The interesting aspect of the anion replacement is that it enables formation of solid solutions at the composition interval $Tl_5Te_{3-x}Hal_x$ $(0<x\leq 1)$. Meantime, Tl gradually

changes its oxidation state by switching to Tl^+ and provides electroneutrality. The analysis of the Tl_5Te_3 type structures show that both Tl_5Te_3 and Tl_5Se_{3-x} compounds, as well as their structural analogues are phases of variable composition with a wide one-sided homogeneity areas.

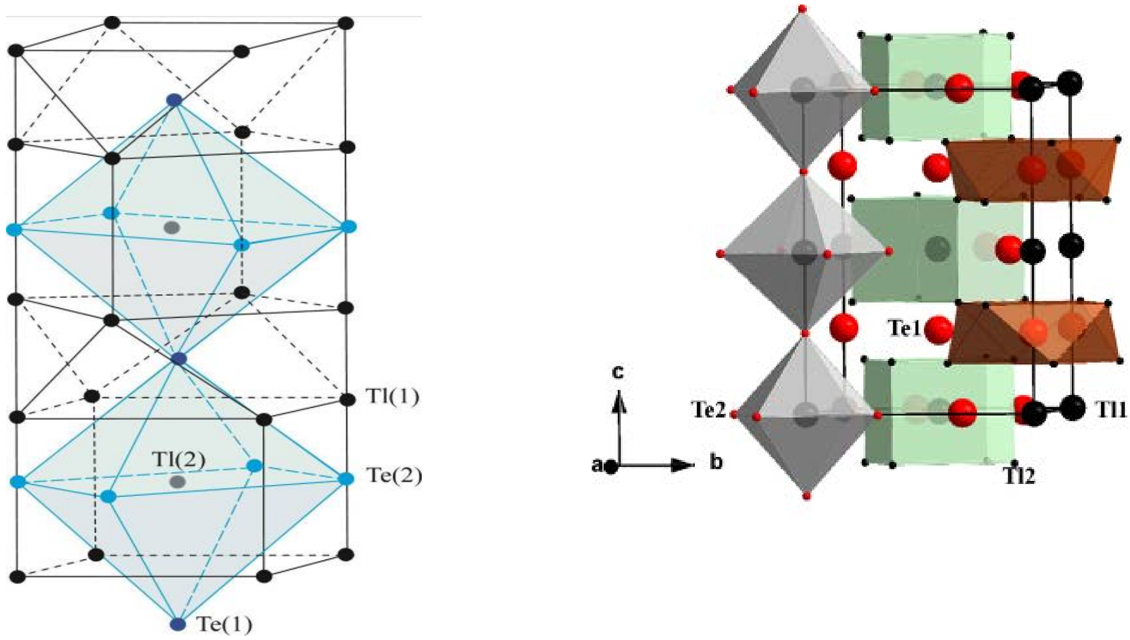


Fig.10. Crystal structure of Tl_5Te_3. The main structural element (a), the projection along the surfaces *b*, *c* (b)

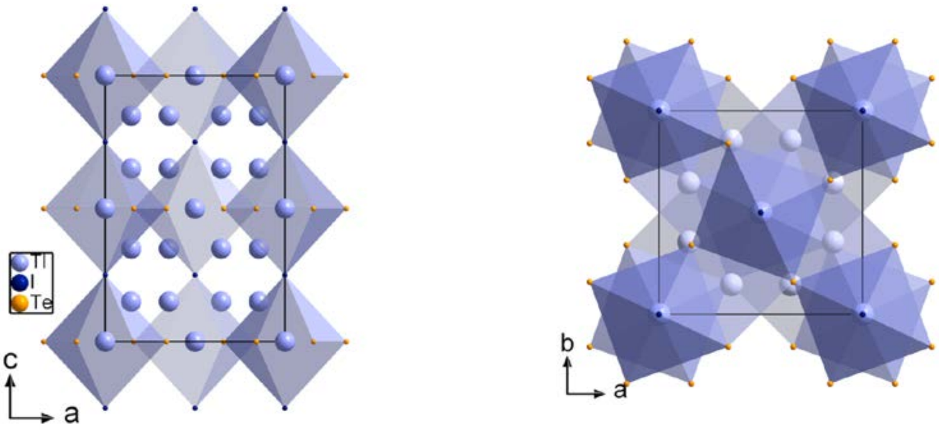
Table 1. Crystal lattice parameters of Tl_5Te_3 and tallium chalcohalides

Compound	Syngony, Space Group	Lattice parameters, Å	Reference
Tl_5Te_3	Tetragonal, I4/mcm	*a=8.930; c=12.598; z=4*	[114]
Tl_6SI_4	Tetragonal, *P4/mnc*	*a=9,176; c=9,608; z=2*	[61,82]
Tl_6SBr_4	“—“	*a=8,721; c=9,328; z=2*	[61,82]
Tl_6SCl_4	“—“	*a=8,830; c=9,170; z=2*	[61,82]
Tl_6SeI_4	“—“	*a=9,178; c=9,675; z=2*	[81,82]
Tl_5Se_2I	Tetragonal, *I4/mcm*	*a=8,663; c=13,463; z=4*	[71]
Tl_5Se_2Br	“—“	*a=8,594; c=12,788; z=4*	[123]
Tl_5Se_2Cl	Tetragonal, *P4/ncc*	*a=8,565; c=12,741; z=4*	[123]
Tl_2TeI_6	Monoclinic, $P2_1/c$	*a=7,765; b=8,174; c=13,756;* $\beta=124,2^0$*; z=2*	[102]
Tl_2TeBr_6	Tetragonal, *P4/mnc*	*a=7,468; c=10,682; z=2*	[102]
Tl_2TeCl_6	Cubic, *Fm-3m*	*a=10,107; z=4*	[124]
Tl_5Te_2I	Tetragonal, *I4/mcm*	*a=9.001; c= 13.291; z=4*	[108]
Tl_5Te_2Br	Tetragonal, *I4/mcm*	*a =8.974; c= 12.812; z = 4*	[125]
Tl_5Te_2Cl	Tetragonal, *I4/mcm*	*a =8.921; c= 12.692; z = 4*	[90,92]

Crystal structure of Tl_5Se_2Hal compounds was studied, their lattice parameters, and positions of atoms in the unit cell determined [71,123]. All of them are crystallized with the In_5Bi_3 structure which is a subfamily of the Cr_5B_3 type: $Tl_5Se_2I(Br)$ is crystallized in the space group *14/mcm*, Tl_5Se_2Cl as a lower symmetric distorted variant in *P4/ncc*. Around one central thallium atom there are slightly distorted octahedra of two halogen and four selenium atoms occur. These octahedra are covered by cubes of thallium atoms. The octahedra are interconnected via common vertices and the cubes via common edges to give the three-dimensional structure [123].

The crystal structure study of $Tl_5Te_2Cl(Br)$ compounds was carried out by the Rietveld method based on powder X-rays analysis. The unit cell parameters and isotropic atomic positions of the atoms were refined by TOPAS-4.2 program [90,125].

Based on the phase diagram of the Tl-Te-I system, it was proposed and implemented an original method of growing single crystals of Tl_5Te_2I which melts incongruently by syntectic reaction [65,126]. The method has been used in order to control the crystallization process from two immiscible liquid phases $L_1 + L_2$. In this method the liquid phase L_1 was in dynamic equilibrium with another liquid phase and the compositions of the coexisting liquid phases always constant at the given temperature. During very slow crystallization from the L_1, the phase L_2 gradually dissolves in L_1, and provides constancy of its composition to form consequently the Tl_5Te_2I by the syntectic reaction at 775 K according to phase diagram.



a) b)

Fig.11. Crystal structure of Tl_5Te_2I : a) view along the [010] direction; b) Projection along the *c*-axis. Tl1 atoms in lighter color.

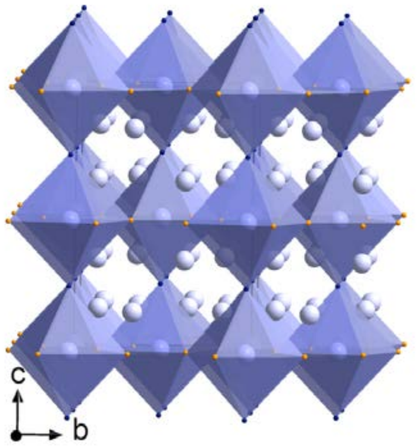


Fig. 12. Perspective view of Tl_5Te_2I showing a layer of Tl_5Te_2I corner-sharing octahedral. Color codes like in Fig. 11 and Tl1 atoms in lighter color

Single crystal X-ray diffraction data was collected at room temperature on a STOE StadiVari diffractometer. The structure was refined using as starting model that of Tl_5Te_3; refinement performed with the program system JANA2006. All atoms were refined with occupancies according to the stoichiometric formula, anisotropic thermal displacement parameters and without any constrain. Images of chemical structure were visualized using VESTA software. Full crystal structure details, data collection and structure refinement details are given in [108]. The structure can be described as layers of corner sharing $TlTe_4I_2$ octahedral (Tl2 central atom) with additional interstitial Tl1 atoms with trigonal prism coordination. Octahedra consecutive along the c-axis are rotated 45 relative to each other. A projection along the [010] and [001] directions, and perspective view of the structure are shown in the Fig. 11 and 12 [127] reported formation mechanism of the anion- and cation substituted anologs of Tl_5Te_3 takes into consideration structural properties of this compound and the electronic structure of thallium. The rational content of these analogues Tl_4BX_3, Tl_9BX_6 and Tl_5X_2Hal was justified, and the reasons for their one-sided stoichiometry determined.

Tl_6SHal_4 and Tl_6SeI_4 (Hal– I,Br,Cl) ternary compounds are crystallized in a tetragonal lattice of the type Tl_4HgBr_6 [61,81,82] (Fig.13). There are two distinct crystallographic sites for Tl cations. Each Tl^+ ion is coordinated with four Hal− ions and one $(S^{2-})Se^{2-}$ ion.

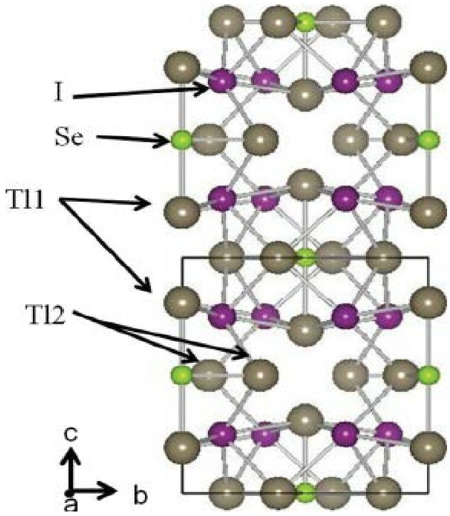


Fig. 13. The crystal structure of Tl_6SeI_4. Two distinct sites for Tl ions are shown as Tl1 and Tl2, respectively [50].

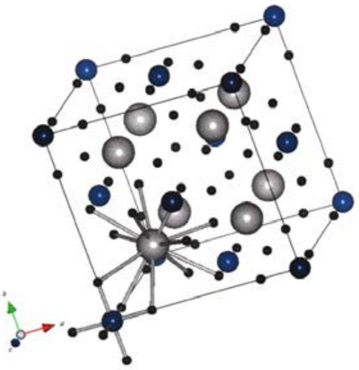


Fig.14. The unit cell of $Tl_2TeBr(I)_6$ compounds. Tl cations are shown by a large gray circles, Te atoms – by dark blue circles and the halogen atoms – by small circles.

The synthesys, identification of the homogeneity areas, growth of monocrystals and study of some properties of the Tl_2TeHal_6 (Hal – I,Br) compounds are reported in [96-102,128-130]. The crystal structure of $Tl_2TeBr_6(I_6)$ compounds was studied in Ref. [98,102] (Fig.14). Both compounds are crystallized in a crystal lattice of the K_2PtCl_6 type. Tl_2TeCl_6 ternary compound crystallize in a cubic unit cell [124] (Table 1).

The methods for the synthesis and monocrystal growth, and some physico-chemical properties of the Tl_6XHal_4 and

Tl_5Se_2Hal chalcohalides were analyzed in Ref. [66,67,78,131,132].

The 3D homogeneity areas were defined and some electrophysical properties of Tl_6SI_4 and Tl_6SeI_4 monocrystals examined in [131,132].

4. Thermodynamic propertis of thallium chalcohalides and related phases

The fundamental thermodynamic characteristics of substances are important to ensure the effectiveness of thermodynamic calculations for optimization of various processes, in particular, conditions for the synthesis and growth of crystals [133, 134].

Thermodynamic propertis of intermediate phases in the Tl-X-Hal systems were excamined through the EMF measurements of the concentration chains

(-) Tl (solid) | gluserol + KlCl + TlCl | (Tl-X-Hal) (solid) (+) (1)

In the chains of type (1), metallic thallium was used as the left electrode, while equilibrium alloys of the Tl-X-Hal systems were used as the right electrodes. A saturated glycerin solution of KCl with the addition of 0.1 mass% TlCl was used as an electrolyte. EMF was measured by the compensation method in the temperature range of 300–430 K and in the 300-380K temperature intervals for sulphur containing systems.

Table 2. Thermodynamic properties of thallium chalcohalides

Compound	$-\Delta_f G^0(298K)$	$-\Delta_f H^0(298K)$	$S^0(298K)$, **(J· mol^{-1}· K^{-1})**	**Reference**
	(kJ·mol^{-1})			
Tl_6SI_4	601.7±2.5	595.1±4.0	672±10	[69]
Tl_6SBr_4	767.0±2.9	790.3±5.2	644±9	[65]
Tl_6SCl_4	833.5±3.7	928.1±14.0	599±9	[64,65]
Tl_6SeI_4	613.1±1.5	609.7±2.6	671±5	[84]
Tl_5Se_2I	341.7±0.8	345.3±2.5	449±8	[84]
Tl_5Se_2Br	374.3±1.0	384.3±2.7	447.6±6.4	[77]
Tl_5Se_2Cl	392.8±1.1	421.6±5.1	433.9±7.2	[72]
Tl_5Te_2I	300.4±1.3	301.1±2.3	475.8±6.6	[104]
Tl_5Te_2Br	340.6±1.6	344.5±2.7	483.4±6.2	[95]
Tl_5Te_2Cl	355.9±1.1	377.1±5.0	474.1±6.8	[92]

The homogeneity areas of phases were refined, the relative partial molar functions of thallium in alloys and the integral thermodynamic functions of thallium chalcohalides and solid solutions based on them calculated on the basis of the results of EMF measurements of the chains type (1). The standard thermodynamic functions of formation and the standard entropies of ternary thallic chalco-halides are summarized in the Table 2.

The results of EMF measurements devoted to the determination of homogeneity areas of the Tl_5X_2Hal compounds and calculation of thermodynamic functions of solid solutions are presented and discussed in [84,104,135-138]. As an example, Fig. 15 presents the data of [138] on the refinement of the homogeneity region of the Tl_5Se_2Br compound.

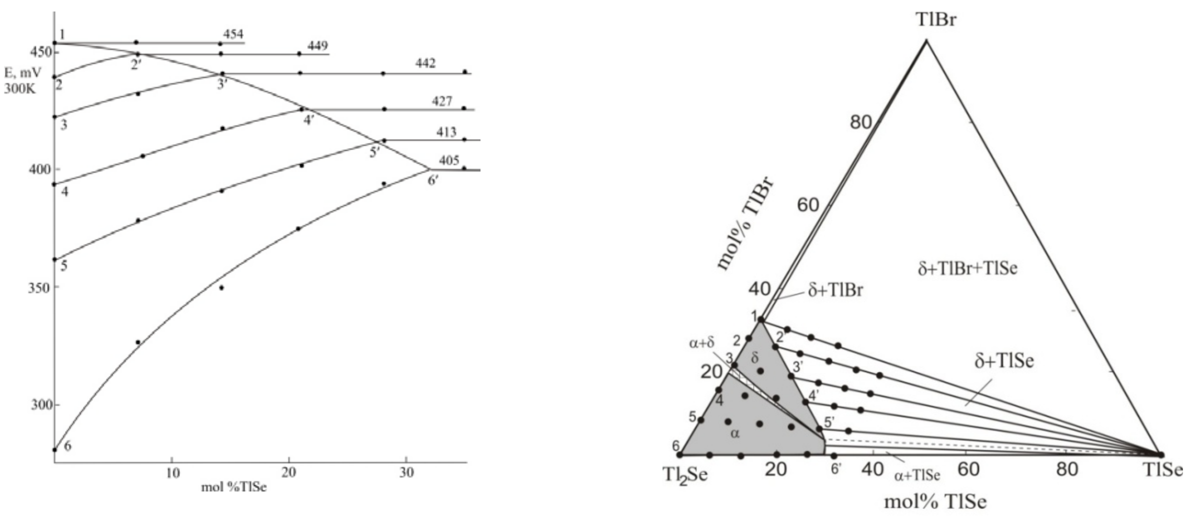


Fig.15. Application of the EMF method for the determination of homogeneity area of Tl_5Se_2Br compound [138]. a) the concentration dependence of the EMF of chains type (1) for alloys along the ray lines from the vertex TlSe b) a fragment of the phase diagram of the Tl-Se-Br system at 300 K.

The relative parsial thermodynamic functions of tallium in the $Tl_5Te_2Br_xI_{1-x}$ solid solutions at 298K were calculated and their dependence graph upon concentration constructed. It has been established that formation of solid solutions in the Tl_5Te_2Br–Tl_5Te_2I system is not accompanied by significant energy and structural changes, and the formed δ-phase is a solid solution of substraction type [139].

The standard thermodynamic functions of formation and atomization, as well as standard entropies of tallium chalcocahalides and variable phases on their base were calculated on the basis of partial thermodynamic functions of thallium using phase diagrams [140].

By using EMF measurements a regulated complex of thermodynamic properties for the Tl_6SBr_4 compound was obtained. The data regarding the thermodynamic properties of all thallium chalco-halides were systematized and comparatively analyzed. Some correlations between thermodynamic functions of thallium chalco-halides and their binary constituents, as well as the ionization degree of chemical bonding were revealed [141,142].

5. Phase equilibria and physico-chemical properties of intermediate phases in some multi-component systems containing thallium, chalcogen and halogen

Some concentration areas of the Tl- X-X$^{/}$-Hal and Tl-X-Hal-Hal$^{/}$ (X,X$^{/}$- chalcogen; Hal,Hal$^{/}$- halogen) four-component systems are of a significant interest in terms of search and development of scientific basis for designing new multicomponent phases based on thallium chalcohalides. Another way for varying the properties of ternary compounds is to investigate the phase equilibrium in systems composed of them and their structural analogues. In this regard, Tl_5Te_2Hal-$Tl_9B^{V}X_6$ and Tl_5Te_3-Tl_5Te_2Hal-$Tl_9B_VX_6$ systems are very interesting, since all initial constituents of these systems are isostructural thermoelectrics possessing a low thermal conductivity [29].

5.1. Tl–X–X$^/$–Hal (X, X$^/$–chalcogen, Hal–halogen) systems.

The phase equilibria in the systems Tl_2S-Tl_2Se-TlI(Br) were studied, some polythermal sections and the liquidus surface projections of these systems constructed [143,144]. It was shown that, the Tl_6SI_4-Tl_6SeI_4 [145,146] and Tl_2S-Tl_5Se_2I [147] quasi-binary sections divide the Tl_2S-Tl_2Se-TlI system into 3 sub-systems. The Tl_2S-Tl_2Se-Tl_5Se_2I subsystem is of monotectic eutectic type [143] due to the formation of continuous solid solutions along the Tl_6SI_4-Tl_6SeI_4 section [145].

3 monocrystals of the Tl_6SI_4-Tl_6SeI_4 solid solutions were grown by direct crystallization and their some physico-chemical properties studied [148].

The physicochemical interaction of components in the TlI-Tl_6SI_4-Tl_6SeI_4 system was studied by means of DTA and X-ray analysis, the projection of the liquidus surface and the TlI–$Tl_6S_{0,5}Se_{0,5}I_4$ polythermal section of the system were constructed [149]. The monovariant eutectic $L\rightarrow\alpha+\beta^/$ equilibrium curve of the TlI–$Tl_6S_{0,5}Se_{0,5}I_4$ system is calculated based on mathematical modeling.

Three vertical cross sections (Tl_2S-Tl_2Se,Tl_2S-Tl_5Se_2Br, Tl_6SBr_4-Tl_5Se_2Br) and the liquidus surface projection of the Tl_2S-Tl_5Se_2Br-TlBr system were constructed, the boundaries of phase areas, as well as the coordinates of nonvariant equilibriums determined [150].

5.2. Tl–X–Hal–Hal$^/$ systems

The research results of the systems composed of selenides and halides of tallum are reported in [151-153]. It revealed that the TlSe-TlCl-TlI system belongs to the nonvariant eutectic type [151], whereas TlSe-TlBr-TlI [152] and TlSe-TlCl-TlBr [153] are of the monovariant eutectic type.

Tl_5Se_2Br-Tl_5Se_2I and Tl_5Te_2Br-Tl_5Te_2I systems are characterized by formation of continuous solid solutions [154,155].

The interaction between A_2TeC_6 (A–K,Rb,Cs,Tl; C–Br,I) compounds was studied and their T-x diagrams constructed [99,154]. These systems are quasi binary and form a phase diagram of eutectic type containing a large solid solution areas on the base of primary constituents.

The effect of the crystallochemical factor on the interaction of the components in these systems was determined by the ratio of the type of A2TeC6 compounds and the extent of the interaction of these cations and their anions in determining the nature of the interaction in these systems.

By the influence of the crystallochemical factor on the interaction of components in these systems it was determined that the main parameter defining the structur type of A_2TeC_6 compounds and the character of chemical interaction in these systems is the size ratio of cations and anions.

The phase equilibria in the T_2Te–TlBr–TlI, Tl_2Te–TlCl–TlI, Tl_2Te–TlCl–TlBr systems were studied by means of DTA and X-ray analysis, as well as by measurement of microhardness and EMF of the concentration chains relative to the thallium electrode [141,157,158]. Some polythermal sections, an isothermal section at 300K, as well as the projection of the liquidus surface of all three systems were constructed. The primary crystallization areas, types and coordinates of non- and monovariant equilibriums determined.

Tl_5Te_2Hal–$Tl_5Te_2Hal^/$ systems are nonquasi-binary due to the incongruent melting character of ternary compounds and consists of aliquation fields. However, isostructural Tl_5Te_2Hal (Hal – Cl, Br, I) compounds form continuous solid solutions in solid state. Thus, a very interesting and rare phenomenon is observed in these systems – despite the fact that, there is a complete aliquation in liquid state, the initial constituents of these systems are completely dissolved in each other in solid state. Realization of a such an unusual phenomenon in the Tl_5Te_2Hal–$Tl_5Te_2Hal^/$ systems is related to the fact that the aliquation in these systems does not reflect the character of interaction between the ternary compounds, but rather the melting character of these compounds and solid solutions based on them [159]. Also the composition of the layered liquid phases is outside of the T-x plane of these systems.

In all Tl_2Te–TlHal–$TlHal^/$ systems, the homogeneity areas of the solid solutions based on the Tl_5Te_2Hal compounds fall outside the Tl_5Te_2Hal–$Tl_5Te_2Hal^/$ sections and occupy a wide area in the Tl_2Te–Tl_5Te_2Hal–$Tl_5Te_2Hal^/$ subsystems. This is due to the existence of a large one-sided homogeneity area on the basis of Tl_5Te_2Hal compounds in the Tl_2Te-TlHal systems.

6. Phase equilibria in some systems consisting of compounds of the Tl_5Te_3 type crystal structure

Tl_5Te_3-Tl_9BiTe_6-Tl_5Te_2Hal systems are of great interest in terms of preparation of thermoelectric materials with very low heat conductivity. The point is that one of the components - Tl_9BiTe_6 compound has a record high thermoelectric efficiency [29]. By incorporating halogen atoms in the crystal lattice of this compound, it is possible to further complicate them and reduce the thermal conductivity.

Phase equilibriums in the Tl_5Te_3-Tl_9BiTe_6-Tl_5Te_2Hal systems were investigated by physico-chemical analysis methods, the isothermal sections at 760 and 800K and the projections of the liquidus surfaces of these systems were consrtucted [160-163].

Tl_5Te_3-Tl_9BiTe_6 and Tl_5Te_3-Tl_5Te_2Hal boundary systems of the Tl_5Te_3-Tl_9BiTe_6-Tl_5Te_2Hal concentration trangles were studied in [83,89,164]. It showed that these systems are characterized by unlimited dissolution of components one into another. Tl_9BiTe_6-Tl_5Te_2Hal systems form a continuous solid solutions (δ-phase) and are quasi-binary due to the incongruent melting of tellurohalides [163]. The composition of liquid phases go beyond the T-x diagram of these systems. Powder diffractograms of all aloys have a Tl_5Te_3 type tetragonal structure while the dependence of lattice parameters on the composition is almost linear.

The liquidus surfaces of the Tl_5Te_3-Tl_9BiTe_6-Tl_5Te_2Hal systems are composed of two parts matching to the primary crystallization of δ-phase from the homogeneous alloy and $L+L_1$ immiscibility area. The *ab* curve connecting these two regions is characterized by the $L+L_1 \rightarrow \delta$ monovariant syntectic equilibrium. The solidus of the system consists of a surface to comply with the end of crystallization (dashed line) [160-162]. The liquidus projection of all three systems is qualitatively similar and differs only by the size of the $L+L_1$ immiscibility area. The results on the phase equilibrium can be used to select the composition of the sample and temperature regimes when growing δ-solid solution crystals of given composition [159].

Conclusion

In the review paper, the literature data and results of the work of the authors on physico-chemical research into some ternary and more complex systems which are considered important in terms of creation of physico-chemical bases for directional synthesis of tallium chalcohalides and related multicomponent non-stoichiometric phases. It revealed that as a result of the studies in these systems, a wide range of ternary compounds and multicomponent solid solutions of great interest as promising functional materials with thermoelectric, optical, magnetic, sensor and detector properties were identified. These data open up great opportunities for optimizing the functional properties of phases by directional variation of their composition. Besides, the fundamental thermodynamic properties of thallium chalcohalides and many phases of variable composition which are valuable as scientific data and important for optimizing conditions of their design were determined.

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TALLİUMUN XALKOHALOGENİDLƏRİ ƏSASINDA ÜÇLÜ VƏ DAHA MÜRƏKKƏB FAZALARIN ALINMASININ FİZİKİ-KİMYƏVİ ASPEKTLƏRİ

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İcmal məqalədə talliumun xalkohalogenidlərinin və onlar əsasında yeni çoxkomponentli fazaların alınması baxımından maraq kəsb edən bəzi üçlü və daha mürəkkəb sistemlərin fiziki-kimyəvi tədqiqinin nəticələri sistemləşdirilmiş və təhlil edilmişdir. Qeyri-üzvi maddələrin bu sinfi termoelektrik, optik, maqnit, sensor və detektor xassələrinə malik olan perspektivli funksional materiallar kimi elmi və praktiki maraq kəsb edir. Burada həmçinin, tallium xalkohalogenidlərinin və onlar əsasında dəyişən tərkibli aralıq fazaların kristal quruluş xüsusiyyətləri, termodinamik və bəzi fiziki-kimyəvi xassələrinə aid ədəbiyyat məlumatları araşdırılmışdır.

Açar sözlər: *tallium xalkohalogenidləri, funksional materiallar, faza diaqramı, bərk məhlullar, termodinamik xassələr, kristal quruluş.*

ФИЗИКО-ХИМИЧЕСКИЕ АСПЕКТЫ РАЗРАБОТКИ ТРОЙНЫХ И СЛОЖНЫХ ФАЗ НА ОСНОВЕ ХАЛЬКОГАЛОГЕНИДОВ ТАЛЛИЯ

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В обзоре систематизированы и проанализированы результаты физико-химических исследований тройных и более сложных систем, представляющих интерес с точки зрения получения халъкогалогенидов таллия и новых многокомпонентных фаз на их основе. Этот класс неорганических веществ представляет научный и практический интерес как перспективные функциональные материалы с термоэлектрическими, оптическими, магнитными, сенсорными и детекторными свойствами. Также проанализированы литературные данные о кристаллической структуре, термодинамических и некоторых физико-химических свойствах халькогалогенидов таллия и фаз на их основе.

Ключевые слова: *халькогалогениды таллия, функциональные материалы, фазовая диаграмма, твердые растворы, термодинамические свойства, кристаллическая структура.*