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# The phase equilibria in the Tl-S-I system and electrical properties of the Tl<sub>6</sub>SI<sub>4</sub> and TlS compounds

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#### Abstract

The phase equilibria in the ternary Tl-S-I system were investigated experimentally by means of powder X-ray diffraction (PXRD) and differential thermal analysis (DTA). Five isopleth sections, liquidus surface projection and room temperature isothermal section were constructed based on experimental data. *dc*-and *ac*-electric properties of the TIS and Tl<sub>6</sub>SI<sub>4</sub> crystals were studied within the temperature and frequency ranges from 120 K to 300 K and from 50 kHz to 35 MHz, respectively. The hopping mechanism for charge transfer over the localized states near the Fermi level was established at low temperatures and high frequencies for these compounds. The density and energy scatter of the states which are located in the vicinity of the Fermi level as well as the average time and distances of jumps were estimated for the title compounds.

**Keywords**: chalcohalides; phase equilibria; ternary systems; radiation detectors; electric measurements; localized states.

#### 1. Introduction

Chalcogenides and chalcohalides of Group III-V metals are of potential interest as prospective materials for new generation of electronic and spintronic devices thanks to their wide range of electronic properties such as semiconducting, thermoelectric, photoelectric ones, etc. [1, 2]. The binary and ternary thallium containing phases take an important place among these materials with outstanding electronic properties [3-10] in spite of toxicity of thallium compounds.

The Tl–S–I system belongs to a group of alloy systems considered as promising materials for efficient X-ray and  $\gamma$ -ray detection, e.g., the ternary compound Tl<sub>6</sub>SI<sub>4</sub> displays a higher figure

of merit than the  $Cd_{0.9}Zn_{0.1}Te$  (CZT) crystals which is a current state-of-the-art material for room-temperature operation in X- and  $\gamma$ -ray detection [11-16].

In order to select novel functional materials and to develop chemical foundations of the synthesis conditions, it is crucially important to study the respective phase diagrams. In particular, the synthesis of non-stoichiometric or incongruently melting phases and growth of their single crystals requires the knowledge on the phase diagrams.

The phase equilibria and thermodynamic properties of the systems TI-TIX-Q (X=Cl, Br, I; Q=S, Se, Te) have been carefully investigated in our previous works [3-7]. A number of isopleth and isothermal sections, as well as the liquidus surface projections were constructed. The homogeneity fields of all the intermediate phases were determined and their fundamental thermodynamic functions were calculated from EMF measurements data.

Here, we present a further study of the Tl–S–I ternary system in order to reveal the phase relationships over the entire composition range to provide more accurate experimental data for pure and high-quality materials.

The phase equilibria in the system Tl–S–I were investigated by several authors [4, 17-21] so far. The formation of the congruently melting (715 K)  $Tl_6SI_4$  and  $Tl_3SI$  which are stable within 640-670 K temperature range was reported in Ref. [17]. According to [18],  $Tl_6SI_4$  melts congruently at 710 K and has ~4 mol% homogeneity area (~2 mol % according to [19]). The eutectics contain 7 and 45 mol%  $Tl_2S$  and form at 685 and 665 K, respectively [18]. These data slightly differ from those given in [17] reporting 10 and 45 mol%  $Tl_2S$  at 694 and 670 K, respectively.

The synthesis and single crystal growth methods and conditions, dissociation characteristics as well as other properties of the Tl<sub>6</sub>SHal<sub>4</sub> were reported elsewhere [19, 20].

The phase equilibria in the TI-TII-S subsystem of the title ternary system were investigated experimentally in our previous work [5]. The primary crystallization areas of  $Tl_6SI_4$  and  $Tl_3SI$ , as well as types and coordinates of all non- and monovariant equilibria in the TI-TII-S subsystem were correctly determined. The fundamental thermodynamic properties of the  $Tl_6SI_4$  were accurately calculated from EMF measurements data.

Natural defects present in  $Tl_6SI_4$  single crystals were studied by low-temperature photoluminescence (PL) and photoconductivity (PC) measurements by Peters and co-authors [21]. Large emission band localized at 1.64 eV was observed at low temperatures in the PL measurements. The deep donor level located at 0.46 eV below the conduction-band edge was detected in PC measurements, which agrees well with PL spectroscopy data.

The phase diagrams of the boundary binary systems Tl-S, Tl-I are adopted from Ref. [22] whereas, the S-I one is taken from [23].

The system Tl-S includes binary compounds  $Tl_2S$ ,  $Tl_4S_3$ , TlS,  $Tl_2S_5$  and  $Tl_2S_3$  [22].  $Tl_2S$  melts congruently at 728 K whereas,  $Tl_4S_3$ , TlS, and  $Tl_2S_5$  compounds form by peritectic reactions at 570, 505 and 397 K, respectively.  $Tl_2S_3$  decomposes by the solid phase reaction  $Tl_2S_3 \rightarrow TlS + Tl_2S_5$  at ~370 K.

So far, three binary compounds, namely - TII, TII<sub>3</sub> and Tl<sub>3</sub>I<sub>4</sub> were found in the Tl-I system [22]. Thallium monoiodide melts congruently at 715 K and undergoes the TII<sub>I</sub> $\leftrightarrow$ TII<sub>II</sub> polymorph transformation at 451 K. TII<sub>3</sub> and Tl<sub>3</sub>I<sub>4</sub> are formed by peritectic reaction at 402 K and 533 K, respectively.

The S–I system was reported to be a simple eutectic system [23]. The eutectic is located at 338 K and contains ~ 80 at.% S.

Crystal lattice parameters of all phases in the Tl-S-I system are summarized in the Table 1.

#### 2. Experimental

#### 2.1. Synthesis

High purity elemental components (Tl, 99.999%, Alfa Aesar; S, 99.999%, Alfa Aesar; I, 99% resublimed pearls, PA-ACS) were used for the synthesis of starting compounds.

Because of thallium and its compounds are often toxic and quickly oxidized, working with them in laboratory conditions requires a special attention and caution. Therefore, we used protective gloves and laboratory coats both during the sample preparation and measurements processes. The samples are weighed as quickly as possible using an analytical balance to minimize oxidation in air and were then accurately placed into quartz ampoules.

Tl<sub>2</sub>S was prepared from the stoichiometric amounts of the corresponding elements by onestep melting in vacuum-sealed silica tubes ( $\sim 10^{-2}$  Pa) at 800 K, followed by furnace cooling. TlS (503 K) and Tl<sub>4</sub>S<sub>3</sub> (570 K) were slowly cooled after fusing and then annealed for 500 h at 470±5 K and 540±5 K, respectively, because of their incongruent melting character.

Thallium iodides were synthesized by a specially designed method due to high volatility of iodine at high temperatures. The synthesis was performed in an inclined two-zone furnace. The optimal temperature of the hot zone was 20÷30 K higher than the corresponding melting point of the compound, whereas the stable temperature of the cold zone was kept at 400 K. After the most of iodine had reacted, the ampoule was relocated into the hot zone. The melt was incessantly stirred at this temperature by shaking of ampoules. As thallium monoiodide forms by dystectic reaction, it was cooled in the switched-off furnace. However, incongruently melting thallium triiodide was further annealed for 500 h at temperature 20 K lower than the corresponding peritectic temperature.

As there are some disagreemets between the published data on existing intermediate phase between TII and TII<sub>3</sub>, we have synthesized two alloys,  $Tl_2I_3$  and  $Tl_3I_4$ , using TII and iodine. Syntheses were carried out in the evacuated quartz ampoules placed in a two-zone horizontal furnace. A "cold" zone (~300 K) was a source of iodine vapor, while a "hot" zone (~500 K) was used as the reaction area. The fine sintered powder of the thallium monoiodide was in the "hot" zone and continuously reacted with iodine. During the process, substances in the reaction area were stirred by continuous rotation of the ampoules along the longitudinal axis. After the complete adsorption of iodine by the thallium monoiodide occured, the ampoule was placed into the "hot" zone and kept at 500 K for 200 h, then cooled down in the switched-off furnace.

The PXRD analysis of the Tl<sub>2</sub>I<sub>3</sub> alloy shows that its XRD pattern displays diffraction lines identical with that observed in [28]. However, the diffraction pattern of the Tl<sub>3</sub>I<sub>4</sub> contains the most intense lines of the low-temperature modification of TlI ( $2\theta$ =26.73;  $2\theta$ =33.25<sup>0</sup>) together with the reflections of Tl<sub>2</sub>I<sub>3</sub>. The DTA heating curves of the obtained samples contain thermal effects corresponding to the transformation of Tl<sub>2</sub>I<sub>3</sub> (535 and 650 K) and Tl<sub>3</sub>I<sub>4</sub> (535 and 673 K). The comparison of the DTA (Fig. 1*a*) and PXRD data (Fig. 2*a*) with the Tl-I phase diagram [22] confirm that the intermediate thallium iodide is the Tl<sub>2</sub>I<sub>3</sub> and that it melts peritectically at 535±2 K.

The ternary  $Tl_6SI_4$  compound was synthesized by melting appropriate amounts of the presynthesized TII and  $Tl_2S$  in the vacuum-sealed quartz ampoule at ~750 K. The heating curve of  $Tl_6SI_4$  consists of only visible peak corresponding to its melting temperature (Fig. 1b).

All the investigated samples (total weight, 0.5 g) were prepared from initial elements or preliminary synthesized compounds. After the melting process, most of the alloys were annealed at 20-30 K below the solidus temperature for 800-1000h.

#### 2.2. Analysis by DTA and PXRD

DTA and PXRD were used to examine the alloy samples. Thermal analyses of the annealed alloys were carried out using a NETZSCH 404 F1 Pegasus system. The measurements were performed from room temperature up to 800 K depending on sample composition with a heating and cooling rate of 10 K min<sup>-1</sup>. Temperatures of thermal effects were taken mainly from the heating curves.

The PXRD analyses were performed on a Bruker D8 ADVANCE diffractometer with the Cu-K $\alpha_1$  radiation. The lattice parameters were refined using the Topas V4.2 software. PXRD confirmed that the pre-synthesized binary and ternary compounds were phase-pure, and the unit cell parameters perfectly agreed with the literature data. The PXRD pattern of the Tl<sub>6</sub>SI<sub>4</sub> compound was indexed and lattice parameters were calculated. It was confirmed that Tl<sub>6</sub>SI<sub>4</sub>

crystallizes in the Tl<sub>6</sub>HgBr<sub>4</sub> type tetragonal symmetry with the crystal lattice parameters a= 9.1914(9), c = 9.6225(10) Å, and z = 4 which are very close to the literature data [17] (Fig. 2b).

#### 2.3. The dc- and ac-conductivity measurements

The *dc*-electrical measurements were performed in the temperature range from 120 to 286 K for the title compounds placed into a cryostat having a temperature stabilization system. The silver conductive paste was served as a contact material. The thickness of the examined crystals and the contact area were 100–120  $\mu$ m and ~2×10<sup>-2</sup>·cm<sup>2</sup>, respectively. The *dc* electric field applied to the sample varied in the range of 8×10<sup>2</sup>÷ 1.25×10<sup>4</sup> V/cm.

The samples for the *ac*-electric measurements were prepared in the form of parallel plate capacitors. Silver conductive paste served as capacitor plates in this case. The thickness of the samples was 0.1 cm, and the plate area was 0.1 cm<sup>2</sup>. The conductivity of the TIS and  $Tl_6SI_4$  crystals was measured by the resonance technique. The frequency range of the *ac* electric field was  $5 \times 10^4 - 3.5 \times 10^7$  Hz. All the *ac*-electric measurements were carried out at 300 K. The amplitude of the *ac* electric field applied to the samples corresponded to the ohmic region of the current–voltage characteristics.

#### 3. Results and discussion

A full scheme of phase equilibria in the TI-S-I system has been obtained based on experimental and reference data on the boundary binary TI-S [22], TI-I [22], S-I [22] systems and TI-S-I sub-system [6].

For the convenience of comparison, the quasi- and non-quasi-binary isopleth sections are expressed using the normalized compositions, meaning that the number of atoms in initial components is equal.

#### 3.1. The quasi-binary system TII-S

The system is characterized by the monotectic and eutectic equilibria (Fig. 3). A wide twophase liquation field  $L_2+L_3$  covering the area from 2 to 97 at.% S is observed at monotectic  $L_2 \leftrightarrow L_3+(TII)_{II}$  equilibrium (m<sub>4</sub>) temperature (712K). The horizontal line at 450 K reflects the  $(TII)_{I} \leftrightarrow (TII)_{II}$  polymorphic transition. The coincidence of the thermal effects at around 450 K for pristine TII and alloys indicates a negligible solubility range for both modifications of this compound. The crystallization process finishes at 385 K by the eutectic  $L_3 \leftrightarrow (TII)_{I}+S$  reaction (e<sub>9</sub>) and consequently, system transfers into  $(TII)_{I}+S$  two-phase state. The X-ray analysis further confirms this transformation by the appearance of the diffraction lines belonging to the low-temperature modification of thallium monoiodide and elemental sulfur (Fig. 4).

#### 3.2. The 300 K isothermal section of the TI-S-I system

The PXRD data for the selected samples of the TII-I-S subsystem and literature data [7, 18-22] allowed us to plot the isothermal section of the TI-S-I system at 300 K (Fig. 5). The only one ternary compound, namely  $Tl_6SI_4$ , has been found in this system. The thallium monoiodide, which is the most thermodynamically stable compound of the system, is in equilibrium with all phases except of the  $Tl_4S_3$  phase. On the other hand, all three thallium iodides are in tie line connection with elemental sulfur. This leads to the formation of the three-phase areas in the TI-S-I system.

#### 3.3. The liquidus surface projection of the Tl-S-I system

The liquidus surface projection of the system is illustrated in the Fig. 6 while the types and coordinates of all non- and monovariant equilibria are summarized in Tables 2 and 3. The liquidus surface consists of twelve primary crystallization fields. The primary crystallization fields of thallium, sulfur and  $Tl_2S_5$ , as well as several equilibrium points and curves are found to be degenerated at the thallium and sulfur corners of the concentration triangle. These areas are represented by blow-ups in Figs. 6 *a,b,c*.

The largest primary crystallization area in the system belongs to high-temperature modification of the thallium monoiodide (TII)<sub>II</sub>. This area covers most of non- and mono-variant equilibria in the TI-S-I system (Tables 1 and 2). The ternary  $Tl_6SI_4$  compound has also a wide primary crystallization area, which allows to growing its large single crystals from nonstoichiometric melts. The primary crystallization field of the  $Tl_3SI$  compound ( $M_3P_6U_7e_2M_2U_5$ ) exists in a narrow temperature interval from 640 to 670 K [6] (Fig. 6). Despite the fact that this compound decomposes by the  $Tl_3SI \rightarrow Tl_2S + Tl_6SI_4$  solid-state reaction [17] along the section  $Tl_2S$ -TII, its decomposition occurs by transition reactions U<sub>5</sub> and U<sub>7</sub> (Table 2) beyond this section. The notable feature of the Tl-S-I system is the presence of two wide  $L_1+L_2$  and  $L_2+L_3$ immiscibility regions (L<sub>1</sub> is the melt based on metallic thallium, L<sub>2</sub> is the liquid solution of sulfides, iodides and thallium triiodide,  $L_3$  is the melt based on of sulfur and iodine). The  $L_1+L_2$ area almost entirely covers the Tl-Tl<sub>2</sub>S-TlI subsystem, however, the L<sub>2</sub>+L<sub>3</sub> area takes a considerable part at the center of the composition triangle. The latter liquation area comes from quasi-binary TII-S section (Fig. 3), then it penetrates into the iodine-  $(m_4M_5K_2M_5'm_4')$  and sulfur-rich  $(m_4M_5K_2M_5m_4)$  areas (Fig. 6). The primary crystallization fields of all the phases are bordered by the monovariant curves (Table 3) and nonvariant points (Table 2). The monovariant eutectic and peritectic curves are transformed into the nonvariant monotectic equilibria upon the intersection with immiscibility areas (See Fig. 6 and Table 3, the conjugate pairs of  $M_1M_1'$ ,  $M_2M_2'$ ,  $M_3M_3'$ ,  $M_4M_4'$ ,  $M_5M_5'$  points).

#### 3.4. Isopleth sections

The phase diagrams of the  $Tl_2I_3$ -S,  $TlI_3$ -S,  $TlI_{0.5}S_{0.5}$ -I systems (Figs.7-10) intersect all the phase regions in the Tl-S-I system and include the majority of non- and monovariant equilibria. Comparative analysis of these phase diagrams with Fig. 6 and Table 2 and 3 shows excellent agreement between them.

#### 3.4.1. The isopleth section Tl<sub>2</sub>I<sub>3</sub>-S

This section is stable in the subsolidus area (Fig. 7), however, it is entirely non-quasi binary due to incongruent melting character of the  $Tl_2I_3$ . The liquidus of this system consists of only one curve corresponding to the primary crystallization of thallium monoiodide. The comparison of the Fig. 6 and 5 shows that the (TII)<sub>II</sub> crystallizes in a wide composition range from ~5 to 95 at.% S by monovariant monotectic reaction. The thermal effect at 525 K reflects the nonvariant monotectic equilibrium (see Table 2, point M<sub>5</sub>). The polymorphic transition of thallium monoiodide occurs at 450 K. Finally, the crystallization in the Tl<sub>2</sub>I<sub>3</sub>-S section finishes by the U<sub>7</sub> transition reaction at 355 K.

#### 3.4.2. The isopleths section TII<sub>3</sub>-S

This section is also featured by the formation of a large immiscibility region (Fig.8). Hightemperature modification of thallium monoiodide primarily crystallizes from L<sub>2</sub>, L<sub>3</sub> and L<sub>2</sub>+L<sub>3</sub> liquid phases. Then, the crystallization process continues by monotectic reaction M<sub>5</sub> and finishes by the formation of the three-phase area L<sub>2</sub>+L<sub>3</sub>+Tl<sub>2</sub>I<sub>3</sub>. When decreasing the temperature, the L<sub>2</sub> phase completely crystallizes into Tl<sub>2</sub>I<sub>3</sub> and then forms two-phase area L<sub>3</sub>+Tl<sub>2</sub>I<sub>3</sub>. In the 0-80 at.% S compositional range, crystallization occurs by peritectic reaction P<sub>5</sub>U<sub>8</sub> (Table 3) whereas, it continues by the eutectic scheme of L $\leftrightarrow$ Tl<sub>2</sub>I<sub>3</sub>+S within the 80-100 at.% S compositional range. The crystallization ends by a transition equilibrium (see Table2, U<sub>8</sub>) at 345K and the system transforms into the TlI<sub>3</sub>+S two-phase state (Fig.8).

#### 3.4.3. The isopleth section TII-[SI]

The liquidus of the system (Fig.9) consists of four curves according to the primary crystallization of the (TII)<sub>II</sub>, Tl<sub>2</sub>I<sub>3</sub>, TII<sub>3</sub> and iodine. The liquidus curve of the (TII)<sub>II</sub> is almost completely miscible, however, the liquidus of the Tl<sub>2</sub>I<sub>3</sub> partially passes through the immiscibility  $L_2+L_3$  region. The primary crystallization of the TII and Tl<sub>2</sub>I<sub>3</sub> takes place by monovariant monotectic reactions  $L_2\leftrightarrow L_3+(TII)_{II}$  and  $L_2\leftrightarrow L_3+Tl_2I_3$ , respectively at 27-98 mol% and 20-27 mol% TII (Table 3).

The horizontal lines at 525 and 475 K reflect the nonvariant monotectic reaction (M<sub>5</sub>) (Table 2) and the end of the monovariant monotectic reaction  $L_2 \leftrightarrow L_3 + Tl_2I_3$ , respectively. The reaction

 $M_5$  takes place with an excess of the L<sub>2</sub> phase in the < 75 mol% TII composition range whereas, it occurs in >75 mol% TII composition range with the excess of (TII)<sub>II</sub>. Therefore, two threephase areas L<sub>2</sub> +L<sub>3</sub>+Tl<sub>2</sub>I<sub>3</sub> and L<sub>3</sub>+(TII)<sub>II</sub> +Tl<sub>2</sub>I<sub>3</sub> appear in the corresponding composition areas. During the cooling, the latter three-phase mixture, the(TII)<sub>II</sub> →(TII)<sub>I</sub> polymorphic transition occurs at 450 K followed by nonvariant transition reaction U<sub>7</sub> (Table 2). The comparison of the given isopleths with Figs. 5 and 6 show that, the crystallization process complete by the nonvariant eutectic (E<sub>4</sub>) and transition (U<sub>8</sub> and U<sub>7</sub>) reactions at 0-33, 33-67 and 67-100 mol% TII compositional ranges, respectively. Subsequently, the following three three-phase areas appear in the subsolidus area: TII<sub>3</sub>+I<sub>2</sub>+S, TII<sub>3</sub>+Tl<sub>2</sub>I<sub>3</sub>+S and (TII)<sub>I</sub>+Tl<sub>2</sub>I<sub>3</sub>+S (Fig. 9).

#### 3.4.4. The isopleth section Tl<sub>0.5</sub>S<sub>0.5</sub> -I

This section (Fig.10) crosses six three-phase areas in the subsolidus area and contains the most of non- and monovariant equilibria in the TI-S-I system. The nature of the phase equilibria along this section is comprehensively discussed in our previous work [6]. Crystallization features of the alloys and phase equilibria in the iodine-rich area are qualitatively similar to the section TII-[SI] (Fig. 9).

#### 3.5. The ac- and dc-conductivity of the TIS and Tl<sub>6</sub>SI<sub>4</sub>single crystals

The presence of the structural defects in thallium chalcogenides such as vacancies and dislocations results in a high density of localized states near Fermi level. The localized states in the band gap are responsible for most electronic processes occurring in semiconductors. Both *dc* and *ac* charge transports in semiconductors at low temperatures and high frequencies proceed via these localized states.

The experimental data obtained in *dc*-electric measurements indicate that the TIS single crystal exhibits variable range of hopping conductivity over states lying in a narrow energy band near Fermi level (Fig. 11) in the temperature range from 120 to 230 K. According to this type of conductivity [33]

$$\sigma \sim \exp[-(T_0/T)^{1/4}],$$
 (1)

where  $T_0 = 16/(N_F \cdot ka_l^3)$ , k is the Boltzmann constant,  $a_l$  is the localization radius.

The density of states near Fermi level for TIS was calculated from the low-temperature dcconductivity measurements:  $N_F = 2.8 \times 10^{20} \text{ eV}^{-1} \text{ cm}^{-3}$ .

Frequency-dependent 300 K *ac*-conductivity of TIS crystal (Fig.12, a) follows the relation  $\sigma_{ac} \sim f^{0.8}$  at  $f \ge 10^6$  Hz. The observed  $\sigma_{ac} \sim f^{0.8}$  behavior in TIS attests to hopping transport through the localized in forbidden gap states [33]:

# ACCEPTED MANUSCRIPT $\sigma_{ac}(f) = \frac{\pi^3}{96} e^2 k T N_F^2 a_l^5 f \left[ \ln \left( \frac{\nu_{ph}}{f} \right) \right]^4, \qquad (2)$

where *e* is the unit charge,  $N_F$  is the density of states near Fermi level,  $a_l = 1/\alpha$  is the localization radius,  $\alpha$  is the exponent of the decay of the wave function  $\psi \sim e^{-\alpha r}$  of the localized charge carrier,  $v_{ph}$  is the phonon frequency. Similar frequency-dependent conductivity was also found for the Tl<sub>6</sub>SI<sub>4</sub> single crystal (Fig. 12, b). The Fermi level density of states ( $N_F = 3.1 \times 10^{19} \text{ eV}^{-1} \text{ cm}^{-3}$  for TlS and  $N_F = 2 \times 10^{18} \text{ eV}^{-1} \text{ cm}^{-3}$  for Tl<sub>6</sub>SI<sub>4</sub>) have been evaluated. The  $v_{ph}$  in the crystals under study was taken to be  $10^{12}$  Hz [34]. The spread of energies near Fermi level was calculated by following formula [35]:

$$\Delta W = 3/2\pi R^3 \cdot N_F \tag{3}$$

 $(\Delta W = 2.4 \times 10^{-3} \text{ eV} \text{ for TlS and } 4.1 \times 10^{-2} \text{ eV} \text{ for Tl}_6\text{SI}_4)$ , and the mean hop distance (R = 185 Å for TlS and R = 180 Å for Tl}6SI\_4) have been estimated by following formula [35]:

$$R = \frac{1}{2\alpha} \ln \left( \frac{v_{ph}}{f} \right).$$
(4)

#### 4. Conclusion

Experimental data from DTA and PXRD measurements allowed us to obtain a selfconsistent description of phase relationships in the Tl-S-I system. The plotted phase diagram presents valuable information useful to achieve controlled synthesis of the materials with desired compositions and growth of bulk single crystals of the title compounds both from stoichiometric and non-stoichiometric melts. Moreover, determination of the eutectic, peritectic and polymorphic phase transformations, as well as the primary crystallization areas and the homogeneity ranges of the existing phases allow to better understand the composition–structure– properties relationships for Tl-S-I alloys.

From electric and high-frequency dielectric measurements, it was found that the *dc*- and *ac*-conductivities of TIS and Tl<sub>6</sub>SI<sub>4</sub> single crystals at low temperatures and high frequencies indicate the hopping mechanism of the charge transfer over the states localized near Fermi level. The density of the states at Fermi level is  $3.1 \times 10^{19} \text{ eV}^{-1} \text{ cm}^{-3}$  for TIS and  $2 \times 10^{18} \text{ eV}^{-1} \text{ cm}^{-3}$  for Tl<sub>6</sub>SI<sub>4</sub>. The energy range ( $\Delta W$ ) is found to be  $2.4 \times 10^{-3}$  eV for TlS and  $4.1 \times 10^{-2}$  eV for Tl<sub>6</sub>SI<sub>4</sub>. The average hopping length is estimated as 185 Å for TlS and 180 Å for Tl<sub>6</sub>SI<sub>4</sub>.

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#### Table 1

| Phase                           | Crystal      | Space              | Crystal lattice parameters, Å |        |        | Z  | Reference |
|---------------------------------|--------------|--------------------|-------------------------------|--------|--------|----|-----------|
|                                 | system       | Group              | a                             | b      | С      |    |           |
| Tl <sub>2</sub> S               | Rhombohedral | R3                 | 12.26                         | -      | 18.29  | 27 | [24]      |
| $Tl_4S_3$                       | Monoclinic   | $P2_{1}/c$         | 7.72                          | 12.98  | 7.96   | 4  | [25]      |
| TIS                             | Tetragonal   | $P4_{1}2_{1}2_{1}$ | 7.803                         | -      | 29.55  | 32 | [26]      |
| $Tl_2S_5$                       | Orthorhombic | $P2_{1}2_{1}2_{1}$ | 6.66                          | 16.70  | 6.538  | 4  | [27]      |
| (TlI) <sub>I</sub>              | Orthorhombic | Amma               | 5.251                         | 4.582  | 12.92  | 4  | [28]      |
| (TII) <sub>II</sub>             | Cubic        | Pm3m               | 4.198                         | -      | -      | 4  | [29]      |
| TlI <sub>3</sub>                | Orthorhombic | Pnma               | 9.436                         | 10.599 | 6.419  | 4  | [30]      |
| Tl <sub>2</sub> I <sub>3</sub>  | Hexagonal    | -                  | 6.188                         | -      | 13.412 | -  | [31]      |
| Tl <sub>6</sub> SI <sub>4</sub> | Tetragonal   | P4/mnc             | 9.176                         | -      | 9.608  | 2  | [32]      |

Crystallographic data for the binary and ternary phases in the TI-S-I system

## Nonvariant equilibria in the Tl-S-I system

Table 2

| Point in the                     | Equilibrium                                       | Composit | T,K    |     |
|----------------------------------|---|----------|--------|-----|
| Figure 5                         |   | S        | Ι      |     |
| <b>D</b> <sub>1</sub>            | $L \leftrightarrow Tl_2S$                         | 33.3     | -      | 728 |
| $D_2$                            | L↔(TlI) <sub>II</sub>                             | -        | 50     | 715 |
| $D_3$                            | $L \leftrightarrow \gamma(Tl_6SI_4)$              | 9.1      | 36.4   | 710 |
| $e_1$                            | $L \leftrightarrow (TlI)_{II} + \gamma$           | 4.3      | 44     | 690 |
| $e_2$                            | L↔γ+Tl <sub>3</sub> SI                            | 15       | 25     | 665 |
| e <sub>3</sub>                   | L↔(TlI) <sub>II</sub> +Tl <sub>II</sub>           | -        | <1     | 575 |
| $e_4$                            | $L \leftrightarrow Tl_2S + Tl_{II}$               | <1       |        | 575 |
| e <sub>5</sub>                   | $L \leftrightarrow \gamma + T l_{II}$             | <1       | <1     | 575 |
| e <sub>6</sub>                   | $L \leftrightarrow TlI_3 + I_2$                   | -        | 89     | 363 |
| e <sub>7</sub>                   | $L \leftrightarrow \ S + I_2$                     | 80       | 20     | 338 |
| e <sub>8</sub>                   | $L \leftrightarrow Tl_2S_5 + S$                   | >99      | -      | 385 |
| e <sub>9</sub>                   | $L \leftrightarrow (TlI)_I + S$                   |          | <1     | 385 |
| $E_1$                            | $L \leftrightarrow (TlI)_{II} + \gamma + Tl_{II}$ | <1       | <1     | 575 |
| $E_2$                            | $L \leftrightarrow Tl_2S + \gamma + Tl_{II}$      | <1       | <1     | 575 |
| $E_3$                            | $L \leftrightarrow (TlI)_I + Tl_2S_5 + S$         | >99      | <1     | 385 |
| $E_4$                            | $L \leftrightarrow TlI_3 + I_2 + S$               | 79       | 20     | 335 |
| $P_1$                            | $L+Tl_2S \leftrightarrow Tl_4S_3$                 | 46       | -      | 570 |
| $P_2$                            | L+ Tl₄S <sub>3</sub> ⇔TlS                         | 55       | -      | 503 |
| P <sub>3</sub>                   | $L + TlS \leftrightarrow Tl_2S_5$                 | 98       | -      | 397 |
| $\mathbf{P}_4$                   | $L + (TII)_{II} \leftrightarrow Tl_2I_3$          | -        | 77     | 535 |
| P <sub>5</sub>                   | $L + Tl_2I_3 {\leftrightarrow} TlI_3$             | -        | 83     | 401 |
| $P_6$                            | $L+Tl_2S \leftrightarrow Tl_3SI$                  | 21       | 19     | 670 |
| $U_1$                            | $L{+}Tl_3SI \leftrightarrow \gamma {+}Tl_2S$      | 26       | 17     | 635 |
| $U_2$                            | $L+Tl_2S \leftrightarrow \gamma+Tl_4S_3$          | 43       | 5      | 560 |
| $U_3$                            | $L+Tl_4S_3\leftrightarrow\gamma+TlS$              | 54       | 2      | 495 |
| $U_4$                            | L+γ↔(TlI) <sub>II</sub> +TlS                      | 60       | 3      | 475 |
| $U_5$                            | $L+Tl_3SI\leftrightarrow\gamma+Tl_2S$             | <1       | <1     | 635 |
| $U_6$                            | $L+TlS \leftrightarrow (TlI)_I +Tl_2S_5$          | 98       | <1     | 395 |
| U <sub>7</sub>                   | $L + (TlI)_I \leftrightarrow Tl_2I_3 + S$         | 85       | 14     | 355 |
| $U_8$                            | $L+Tl_2I_3 \leftrightarrow TlI_3 + S$             | 79       | 20     | 345 |
| $m_1(m_1^{\prime})$              | $L_2 \leftrightarrow L_1 + Tl_2S$                 | 32(4)    | -      | 723 |
| $m_2(m_2)$                       | $L_2 \leftrightarrow L_3 + TlS$                   | 73(97)   | -      | 420 |
| m <sub>3</sub> (m <sub>3</sub> ) | $L_2 \leftrightarrow L_1 + (TlI)_{II}$            | -        | 49(<1) | 714 |
| $m_4(m_4)$                       | $L_2 \leftrightarrow L_3 + (TlI)_{II}$            | 2(97)    | 49(~1) | 712 |
| m <sub>5</sub> (m <sub>5</sub> ) | $L_2 \leftrightarrow L_1 + \gamma$                | 8.8(<1)  | 35(<1) | 705 |
| $M_1(M_1)$                       | $L_2 \leftrightarrow L_1 + (TlI)_{II} + \gamma$   | 4(<1)    | 43(<1) | 682 |
| $M_2(M_2)$                       | $L_2 \leftrightarrow L_1 + Tl_3SI + \gamma$       | 18(<1)   | 20(<1) | 661 |
| M <sub>3</sub> (M <sub>3</sub> ) | $L_2 + Tl_2 S \leftrightarrow L_1 + Tl_3 SI$      | 20(<1)   | 18(<1) | 665 |
| $M_4(M_4)$                       | $L_2+(TlI)_{II} \leftrightarrow L_3+TlS$          | 70(97)   | 2(<1)  | 450 |
| $M_{5}(M_{5})$                   | $L_2+(T I)_{II}\leftrightarrow L_3+T _2I_2$       | 73(14)   | 11(84) | 525 |

**Note:** Index I and II in the formulas indicates the low- and high-temperature modification of Tl and TlI, respectively;  $\gamma$ - is the solid solution on the base of  $Tl_6SI_4$ . Conjugate points of the monotectic equilibria are given in parenthesis.

| Curve in the Figure 5       | Equilibrium                              | Temperature intervals, K |  |  |
|-----------------------------|--|--------------------------|--|--|
|                             |  |                          |  |  |
| $e_1M_1$                    | $L \leftrightarrow (TlI)_{II} + \gamma$  | 690-682                  |  |  |
| $e_1U_4$                    | $L \leftrightarrow (TlI)_{II} + \gamma$  | 690-475                  |  |  |
| $e_2M_2$                    | L⇔γ+Tl₃SI                                | 665-661                  |  |  |
| $e_2U_1$                    | L↔γ+Tl <sub>3</sub> SI                   | 665-635                  |  |  |
| $P_6M_3$                    | L+Tl <sub>2</sub> S↔Tl <sub>3</sub> SI   | 670-665                  |  |  |
| $P_6U_1$                    | $L+Tl_2S \leftrightarrow Tl_3SI$         | 670-635                  |  |  |
| $P_1U_2$                    | $L+Tl_2S \leftrightarrow Tl_4S_3$        | 570-560                  |  |  |
| $U_1U_2$                    | $L \leftrightarrow Tl_2S+\gamma$         | 635-560                  |  |  |
| $P_2U_3$                    | L+ Tl <sub>4</sub> S <sub>3</sub> ↔TlS   | 503-495                  |  |  |
| $U_2U_3$                    | $L \leftrightarrow \gamma + Tl_4S_3$     | 560-495                  |  |  |
| $U_3U_4$                    | $L \leftrightarrow \gamma + TlS$         | 495-475                  |  |  |
| $\mathrm{U}_4\mathrm{K}_1$  | L↔(TII) <sub>II</sub> +TlS               | 475-470                  |  |  |
| $K_1M_4$                    | L+(TlI) <sub>II</sub> ↔TlS               | 470-450                  |  |  |
| $P_4M_5$                    | $L+(TII)_{II}\leftrightarrow Tl_2I_3$    | 535-525                  |  |  |
| ${ m M_5}^{\prime}{ m U_7}$ | $L \leftrightarrow (TlI)_{II} + Tl_2I_3$ | 525-355                  |  |  |
| $e_9U_7$                    | L↔(TlI) <sub>II</sub> +S                 | 385-355                  |  |  |
| $U_7U_8$                    | $L \leftrightarrow Tl_2I_3 + S$          | 355-345                  |  |  |
| $P_5U_8$                    | $L+Tl_2I_3 {\leftrightarrow} TlI_3$      | 401-345                  |  |  |
| $e_6E_4$                    | $L \leftrightarrow TlI_3 + I_2$          | 363-335                  |  |  |
| $e_7E_4$                    | $L {\leftrightarrow} S{+}I_2$            | 338-335                  |  |  |
| $U_8E_4$                    | $L \leftrightarrow S + TlI_3$            | 345-335                  |  |  |
| $m_1M_3$                    | $L_2 \leftrightarrow L_1 + Tl_2S$        | 723-665                  |  |  |
| $m_3M_1$                    | $L_2 \leftrightarrow L_1 + (TlI)_{II}$   | 714-682                  |  |  |
| $m_5M_1$                    | $L_2 \leftrightarrow L_1 + (TlI)_{II}$   | 705-682                  |  |  |
| $m_5M_2$                    | $L_2 \leftrightarrow L_1 + \gamma$       | 705-661                  |  |  |
| $M_3M_2$                    | $L_2 \leftrightarrow L_1 + Tl_3SI$       | 665-661                  |  |  |
| $m_4M_4(m_4'M_4')$          | $L_2 \leftrightarrow L_3 + (TII)_{II}$   | 712-450                  |  |  |
| $m_4M_5(m_4'M_5')$          | $L_2 \leftrightarrow L_3 + (TII)_{II}$   | 712-525                  |  |  |
| $M_4m_2(M_4'm_2')$          | $L_2 \leftrightarrow L_3 + TlS$          | 450-420                  |  |  |
| $M_5K_2(M_5K_2)$            | $L_2 \leftrightarrow L_3 + Tl_2 I_3$     | 525-470                  |  |  |

## Mono-variant equilibria of the Tl-S-I system

*Note:* The labeling of phases is the same as in the Table 2. Degenerated monovariant equilibria near the Tl and S corners of the concentration triangle are not represented. They can be easily determined from the Table 2 and Fig.5.

### **Figure Captions**

Figure 1. DTA heating spectrum of: a) Tl<sub>2</sub>I<sub>3</sub> and, b) Tl<sub>6</sub>SI<sub>4</sub>

Figure 2. PXRD patterns of the compounds: a)  $Tl_2I_3$  and, b)  $Tl_6SI_4$ 

Figure 3. The phase diagram of the TII-S system

Figure 4. PXRD patterns for different compositions of the TII-S system: blue; TII, red; 50%

TlI+50% S, black; S (color online)

Figure 5. The 300 K isothermal section of the Tl-S-I system

Figure 6. The liquidus surface projection of the Tl-S-I system (color online). Primary

crystallization fields are: 1,  $Tl_2S$ ; 2,  $Tl_4S_3$ ; 3, TlS; 4,  $Tl_3SI$ ; 5,  $Tl_6SI_4(\gamma)$ ; 6,  $(TlI)_{II}$ ; 7,  $Tl_2I_3$ ; 8,  $TlI_3$ ; 9,  $I_2$ ; 10, Tl; 11, S and 12,  $Tl_2S_5$ 

**Figure 7.** The isothermal section  $Tl_2I_3$  –S

**Figure 8.** The isopleth section TlI<sub>3</sub>-S

Figure 9. The isoplet section TII-[SI]

Figure 10. The isopleth section  $Tl_{0.5}S_{0.5}$  -I

Figure 11. Temperature dependence of the low-temperature conductivity of a TIS single crystal

Figure 12. Frequency-dependent 300 K ac-conductivity for the TlS (a) and Tl<sub>6</sub>SI<sub>4</sub> (b)















A RANK















- The self-consistent phase diagram of the TI-S-I system is constructed
- The existence of the wide immiscibility fields was revealed
- dc-and ac-electric properties for the TIS and Tl<sub>6</sub>SI<sub>4</sub> crystals were studied