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# Experimental investigation of the $3Tl_2Se + Sb_2Te_3 \leftrightarrow 3Tl_2Te + Sb_2Se_3$ phase diagram

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ABSTRACT

Phase equilibriums were established in the $3Tl_2Se + Sb_2Te_3 \leftrightarrow 3Tl_2Te + Sb_2Se_3$ mutual system mainly by the X-ray powder diffraction and differential thermal analyses, with the aid of microhardness and EMF measurements applied to equilibrated alloys. According to the obtained experimental results the phase diagrams in form of the polythermal section and isothermal section at 300 K as well as the projection of the liquids surface have been constructed. It was found experimentally that the system is mutually reversible and is characterized by a wide solid solubility fields along the $TlSbSe_2$–$TlSbTe_2$ subsystem and within the $Tl_2Se$–$Tl_9SbSe_6$–$Tl_9SbTe_6$–$Tl_2Te$ subsystem. The homogeneity and primary crystallization fields as well as the types and coordinates of non- and monovariant equilibriums were determined. The dependencies of crystallographic parameters, microhardness and EMF values upon the composition are discussed. From the EMF measurements, the partial molar functions of thallium ($\Delta\overline{G}, \Delta\overline{H}, \Delta\overline{S}$) were calculated for the revealed nonstoichiometric quaternary phases.

## 1. Introduction

Complex chalcogenides of heavy *p* metals exhibit properties that make them a good base for creating various functional materials, including thermoelectrics [1–3] and three-dimensional (3D) topological insulators [4,5]. These properties open the opportunity to realize a number of new applications in thermoelectrics, spintronics and quantum computing.

In recent years, phase diagrams of several ternary and quaternary systems consisting of chalcogenides of thallium, antimony and bismuth have been investigated. These systems include $Tl_2S$–$Sb_2S_3$–$Bi_2S_3$ [6], $Tl_2Se$–$Sb_2Se_3$–$Bi_2Se_3$ [7], $Tl_2Te$–$Sb_2Te_3$–$Bi_2Te_3$ [8], $3Tl_2S + Sb_2Se_3 \leftrightarrow 3Tl_2Se + Sb_2S_3$ [9], $3Tl_2S + Bi_2Se_3 \leftrightarrow Tl_2Se + Bi_2S_3$ [10], $3Tl_2S + Bi_2Te_3 \leftrightarrow 3Tl_2Te + Bi_2S_3$ [11] and $3Tl_2Te + Bi_2Se_3$ -$\leftrightarrow 3Tl_2Se + Bi_2Te_3$ [12]. In these systems, new quaternary phases with sizable homogeneity ranges were found and subsequently studied for their physicochemical properties.

Understanding the phase relationships in the corresponding systems is always helpful for the development of relative materials. Specifically, the synthesis and growth of the large single crystals from the melt requires the knowledge of the respective phase diagrams. Quaternary phases are much more complex than ternary ones; at the same time they frequently contain quaternary analogs of known ternary phases but with complex substitutional patterns and wide homogeneity ranges. In many cases these phases represent certain interest as objects for varying and tuning properties of their parent compounds.

Here, we report the results of the complete investigation of phase equilibriums in the $3Tl_2Se + Sb_2Te_3 \leftrightarrow 3Tl_2Te + Sb_2Se_3$ quaternary mutual system hereafter denoted (A). We open this paper with reviewing the necessary literature data on the border systems and compounds in them, follow with the experimental procedure, and then discuss our data on the phase equilibriums, polythermal sections, liquidus surface, and partial molar thermodynamic functions.

### 1.1. Binary compounds

Initial binary compounds $Tl_2Se$, $Tl_2Te$, $Sb_2Se_3$ and $Sb_2Te_3$ forming the $3Tl_2Se + Sb_2Te_3 \leftrightarrow 3Tl_2Te + Sb_2Se_3$ quaternary mutual system all melt congruently at 663, 698, 863 and 895 K, respectively [13,14]. $Tl_2Se$ crystallizes in the tetragonal system, space group *P*4/*n*, $a = 8.54$, $c = 12.71$ Å, $z = 10$ [15], whereas $Tl_2Te$ forms the monoclinic lattice with the following unit cell parameters: $a = 15.662$, $b = 8.987$, $c = 31.196$ Å, $\beta = 100.761°$, $z = 44$ and the space group *C*2/*c* [16]. $Sb_2Se_3$ has the orthorhombic crystal structure, space group *Pbnm*: $a = 11.633$; $b = 11.780$; $c = 3.985$ Å; $z = 4$, whereas $Sb_2Te_3$ crystallizes in the rhombohedral tetradymite type of structure with the unit cell parameters: $a = 4.25$; $c = 30.2$ Å, $z = 9$ [15].

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### 1.2. Quasi-binary border subsystems and ternary compounds

#### 1.2.1. The section $Tl_2Se$–$Tl_2Te$

This quasi-binary section relates to the eutectic type with the limited solid solubility fields based on the initial compounds. The eutectic composition lies at 20 mol% $Tl_2Te$ and 648 K [17].

#### 1.2.2. The section $Tl_2Se$–$Sb_2Se_3$

In our previous work [18], the refined phase diagram of this system was reported. Four ternary compounds, namely $Tl_9SbSe_6$, $Tl_3SbSe_3$, $TlSbSe_2$ and $TlSb_3Se_5$ were confirmed in this system. Two of them $Tl_9SbSe_6$ and $TlSbSe_2$ melt congruently at 725 and 730 K, respectively, whereas $Tl_3SbSe_3$ and $TlSb_3Se_5$ are formed by peritectic reactions at 625 and 740 K, respectively. The compositions of the peritectic points lie at 26 and 70 mol% $Sb_2Se_3$, respectively. The eutectic composition between $TlSbSe_2$ and $Tl_3SbSe_3$ has the melting point of 610 K at 28 mol% $Sb_2Se_3$, whereas the eutectic composition formed by $TlSb_3Se_5$ and $TlSbSe_2$ crystallizes at 705 K and 64 mol% $Sb_2Se_3$.

$TlSbSe_2$ undergoes a phase transition at 665 K. The low temperature modification crystallizes in the monoclinic system, space group $P2_1$ with the following unit cell parameters: $a = 9.137$, $b = 4.097$, $c = 12.765$ Å, $\beta = 111.75°$ [19], whereas the high temperature modification has the orthorhombic crystal structure with the unit cell parameters $a = 9.138$; $b = 23.735$; $c = 4.107$ Å [20]; it presents a disordered variant of the TlI structure type. Olsen and coauthors [21] reported that $Tl_3SbSe_3$ crystallizes in the $Na_3AsS_3$-type cubic structure with the unit cell parameter $a = 9.435$ Å (space group $P2_13$). $Tl_9SbSe_6$ has the $Tl_5Te_3$ type tetragonal crystal structure, space group $P4/n$, with the unit cell parameters $a = 8.539$ and $c = 12.69$ Å [22].

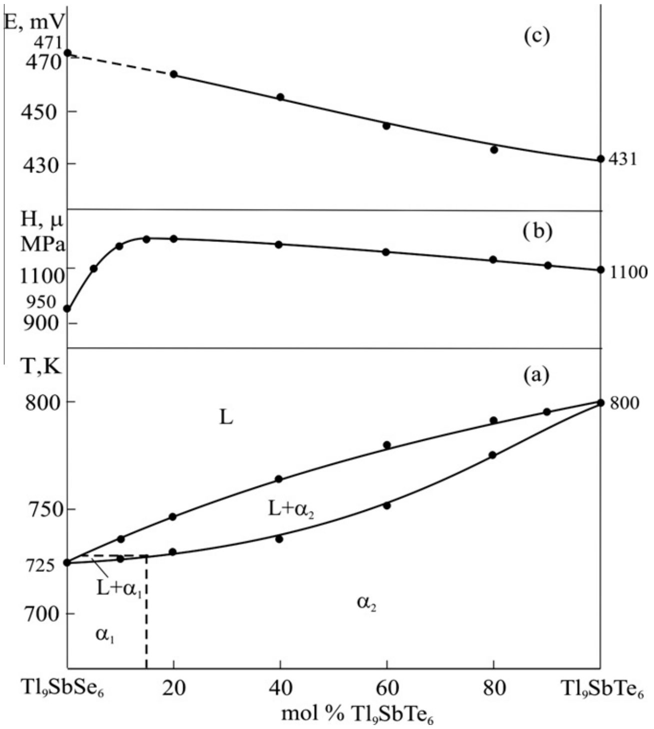

**Fig. 2.** Phase diagram (a), concentration relations of microhardnesses (b) and EMF of the chains of type (1) at 300 K (c) of the system $Tl_9SbSe_6$–$Tl_9SbTe_6$.

#### 1.2.3. The section $Tl_2Te$–$Sb_2Te_3$

This section is characterized by formation of two intermediate ternary compounds $TlSbTe_2$ and $Tl_9SbTe_6$. The former decomposes by a peritectic reaction at 753 K, whereas the latter melts congruently at 798 K and forms a continuous solid solution field with $Tl_2Te$. The solubility in the solid phase based on $Sb_2Te_3$ was found to be about 5 mol% at 753 K. According to the literature [23], $TlSbTe_2$ has the hexagonal crystal structure of the $NaCrS_2$ type with the unit cell parameters $a = 4.425$ and $c = 23.303$ Å. $Tl_9SbTe_6$ is the

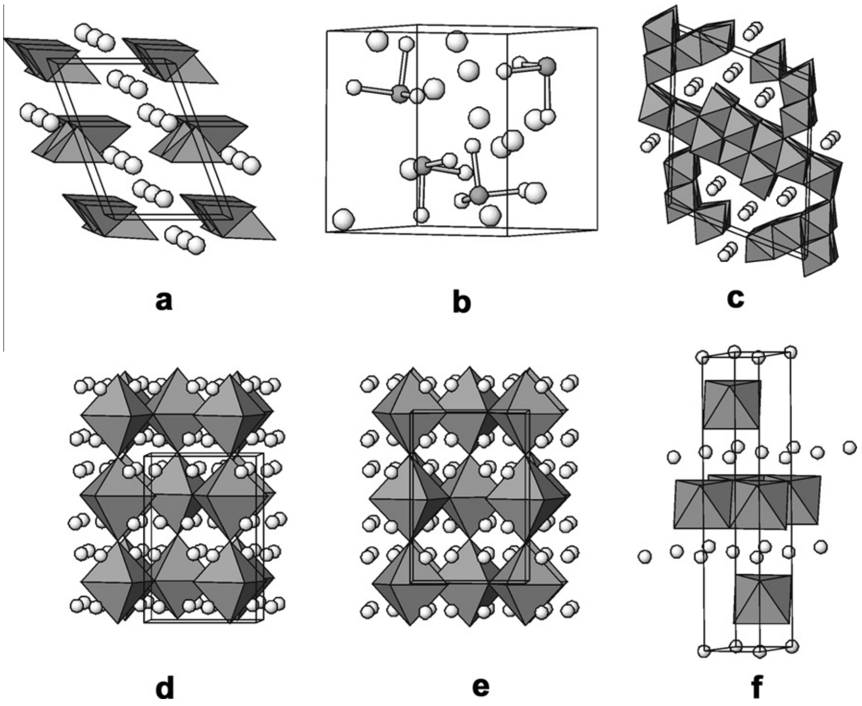

**Fig. 1.** Crystal structures of low-temperature $TlSbSe_2$ (a), $Tl_3SbSe_3$ (b), $TlSb_3Se_5$ (c), $Tl_9SbTe_6$ (d), $Tl_9SbTe_6$ (e), and $TlSbTe_2$ (f). Shown are polyhedra around antimony: square pyramids in (a), pyramids with Sb in a vertex (b), octaherda in all the rest. Thallium atoms are shown as large light spheres.