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SOLID-PHASE EQUILIBRIA DIAGRAM OF THE TL_2TE-TLTBTE$_2$-TLSBTE$_2$ SYSTEM

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Abstract. The phase relations in the Tl_2Te-$TlTbTe_2$-$TlSbTe_2$ composition area of the Tl-Sb-Te-Te quaternary system were investigated by using the differential thermal analysis and powder X-ray diffraction technique. The diagram of solid-phase equilibria at room temperature of this system is constructed. It was determined that the system is characterized by the formation of solid solutions based on $TlTbTe_2$ (β_1-phase), $TlSbTe_2$ (β_2-phase), and δ –phase (continuous solid solutions in the Tl_9TbTe_6-Tl_9SbTe_6 system). Between the above-mentioned phases, the two-phase (β_1+ δ and β_2+ δ) are formed, which are limited by β_1+β_2+ δ three-phase area. The types and lattice parameters of some samples are calculated.

Keywords: *Tl_2Te-$TlSbTe_2$-$TlTbTe_2$ system, phase diagram, solid solutions, powder X-ray diffraction, crystal lattice, topological insulators.*

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1. Introduction

Binary and complex chalcogenides of heavy elements are of great interest as prospective materials possess various functional properties (Ahluwalia, 2016; Alonse-Vante, 2018; Scheer & Schock, 2011; Liu X *et al.*, 2019; Woodrow, 2018).

Although thallium compounds are very poisonous, its chalcogenides attract attention as topological insulators (Banik *et al.*, 2018; Otrokov et al., 2019; Pacile *et al.*, 2018; Pielmeier *et al.*, 2015; Trang *et al.*, 2016; Wang *et al.*, 2015; Eremeev *et al.*, 2010), Weyl semimetals (Ruan *et al.*, 2016; Singh *et al.*, 2012), photodetectors (Piasecki *et al.*, 2017; Barchij *et al.*, 2016), X-ray and gamma radiation detectors (Shi *et al.*, 2017; Das *et al.*, 2017; Lin *et al.*, 2018), and thermoelectric materials (Ding *et al.*, 2018; Shi *et al.*, 2018; Shah *et al.*, 2017).

The insertion of the d- and f- elements into the crystal structure of chalcogenides can upgrade their functional properties and give them additional properties, for example, the magnetic (Sankar *et al.*, 2012; Guo & Kleienke, 2015; Takahashi *et al.*, 2013; Bangarigadu-Sanasy *et al.*, 2014).

The improvement of the functional properties of the above-mentioned compounds materials requires the investigations of the phase diagrams especially systems contain structural analogs because wide areas of solid solutions can be expected into them (Andreev *et al.*, 2015; Babanly *et al.*, 2017, 2019).

In the present paper, we continued our investigations on the phase relations in the systems based on thallium-rare earth elements tellurides. These systems are characterized by the formation of wide areas of solid solutions with the Tl_5Te_3-type structure, which are of practical interest as thermoelectric materials (Imamaliyeva, 2018; Imamaliyeva *et al.,* 2017a,b; 2018a,b,c).

The goal of the present work is the investigation of the solid-phase relations in the Tl_2Te-$TlTbTe_2$-$TlSbTe_2$ system.

The starting binary and ternary compounds, as well as phase equilibria in the boundary systems and the Tl_2Te-Tl_9TbTe_6-Tl_9SbTe_6 subsystem, were studied in a number of papers (Imamaliyeva *et al.,* 2018; Asadov *et al.,* 1977; Cerny *et al.,* 2002; Babanly *et al.,* 1985; Hockings & White, 1961; Duczmal, 2003; Doert & Boetcher, 1994; Bötcher *et al.,* 1997; Botgros *et al.,* 1977; Imamaliyeva *et al.,* 2017 c; Alakbarzade, 2019).

Tl_2Te melts with an open maximum at 698 K (Asadov *et al.,* 1977) and crystallizes in monoclinic lattice structure (Sp.Gr. C2/c; a = 15.662; b = 8.987; c=31.196Å, β=100.76^0, z=44) (Cerny *et al.,* 2002).

$TlSbTe_2$ melts congruently at 753 K (Babanly *et al.,* 1985), and crystallizes in a hexagonal structure (Sp. gr.$R^{-3}m$) with parameters a = 4.425; c = 23.303Å; z = 3 (Hockings & White, 1961).

$TlTbTe_2$ compound is structural analogue of $TlSbTe_2$ and has follow lattice parameters: a = 4.416; c = 24.27 Å; z = 3 (Duczmal, 2003).

According to Ref. (Babanly *et al.,* 1985), the Tl_2Te-$TlSbTe_2$ system is characterized by the formation of the Tl_9SbTe_6 compound with congruent melting at 830 K. This compound crystallizes in tetragonal structure with lattice parameters: a = 8.829, c = 13.001 Å, z=2 (Doert & Bötcher, 1994; Bötcher *et al.,* 1997). Between Tl_2Te and Tl_9SbTe_6, the continuous solid solutions are formed (Botgros *et al.,* 1977). Authors (Babanly *et al.,* 1985) showed, that the system Tl_2Te-Tl_9SbTe_6 is characterized by a morphotropic phase transition near Tl_2Te. Therefore, we re-investigated the phase diagram of the Tl_2Te-Tl_9SbTe_6 system and showed that the system is a quasi-binary system of the peritectic type and is characterized by the formation of limited solid solutions based on the starting components (Imamaliyeva *et al.,* 2018a).

Tl_2Te-$TlTbTe_2$ system is investigated only in the composition interval of ≥80 mol% Tl_2Te. The formation of the Tl_9TbTe_6 compound which melts with decomposition by the peritectic reaction at 780 K and has tetragonal lattice parameters: a=8.871; c=12.973 Å, z=2 was found (Imamaliyeva *et al.,* 2017). Between Tl_2Te and Tl_9TbTe_6, wide solid solutions with Tl_5Te_3 type tetragonal structure are formed (Imamaliyeva *et al.,* 2017c).

The Tl_2Te-Tl_9TbTe_6-Tl_9SbTe_6 subsystem of the Tl_2Te-$TlTbTe_2$-$TlSbTe_2$ system studied by authors of (Imamaliyeva *et al.,* 2018a) is characterized by the formation of wide areas of δ-solid solutions with the Tl_5Te_3 structure occupied more than 90% of the concentration triangle.

Despite the isostructural character of the initial compounds, the $TlSbTe_2$-$TlTbTe_2$ system is characterized by a limited mutual solubility of the initial components: ~30 mol% based on the TlSbTe2 and 10 mol% based on the $TlTbTe_2$ (Babanly *et al.,* 1985). Table 1 presents the parameters of solid solutions in the $TlSbTe_2$-$TlTbTe_2$ system, which we used when discussing the crystallographic data of alloys of subsystem Tl_9SbTe_6-Tl_9TbTe_6 -$TlTbTe_2$-$TlSbTe_2$.

Table 1. Phase compositions and crystallographic parameters of phases of the $TlSbTe_2$-$TlTbTe_2$ (Alakbarzade, 2019)

Compositions % $TlSbTe_2$	**Phase compositions**	**Rhombic lattice parameters, Å**
0 ($TlTbTe_2$)	α	*a* = 4.4245(4); *c* = 23.3025(20)
10	α	*a* = 4.42375 (4); *c* = 23.3751(21)
20	α+β	α – *phase: a* = 4.42374 (4); *c* = 23.3759(21) β – *phase: a* = 4.4180(5); *c* = 24.0061(20)
40	α+β	α – *phase: a* = 4.42376 (5); *c* = 23.3747(21) β – *phase: a* = 4.4183(4); *c* = 24.0024(20)
60	α+β	α – *phase: a* = 4.42375 (5); *c* = 23.3753(21) β – *phase: a* = 4.4184(5); *c* = 24.0052(20)
70	β	*a* = 4.4180(5); *c* = 23.9991(20)
80	β	*a* = 4.4173(4); *c* = 24.1754(20)
90	β	*a* = 4.4165(5); *c* = 24.2516(21)
100	β	*a* = 4.4155(5); *c* = 24.2682(21)

2. Experiments

2.1. Materials and synthesis

Initial binary and ternary compounds were synthesized by direct interaction of the high purity elements, all from Alfa Aesar. The provenance and purity of the elements used are listed in Table 2.

Table 2. Provenance and purity of the materials used in this investigation

Chemical	**Mass fraction of purity**	**CAS No**	**Form**
Tellurium	0.9999	13494-80-9	broken ingots
Antimony	0.99999	7440-36-0	rod, 10-12mm
Terbium	0.999	7440-54-2	foil, 0.1mm
Thallium	0.99999	7440-28-0	rod, 12.7mm

Congruent melt Tl_2Te, Tl_9SbTe_6, and $TlSbTe_2$ compounds were prepared by melting of the elementary components in vacuumed (~10^{-2} Pa) quartz ampoules in a one-zone electric furnace at 850 K. To achieve an equilibrium state, after synthesis, the intermediate ingot of the $TlSbTe_2$ was subjected to heat treatment 700 K for 500 h and cooled in the furnace.

The synthesis of the Tl_9TbTe_6 and $TlTbTe_2$ was carried out by the ceramic method at 1000 K for 100 h. In order to prevent the reaction of terbium with quartz, a graphitized ampoule was used. Then ingots were slowly cooled down to room temperature, crushed in an agate mortar, pressed into pellets and the heating procedure was repeated at 900 K for 500 h.

The purity of the synthesized compounds was controlled by differential thermal analysis (DTA) and powder X-ray diffraction (XRD) techniques.

The intermediate samples of the studied system were prepared by melting of the presynthezed and identified binary and ternary compounds in evacuated quartz tubes at the $30\text{-}50^0$ above the melting point of the compounds followed by cooling in the switched-off furnace. Then samples were annealed at 700 K within 500h.

The one-phase of the synthesized compounds were confirmed by DTA and PXRD technique.

2.2. Methods

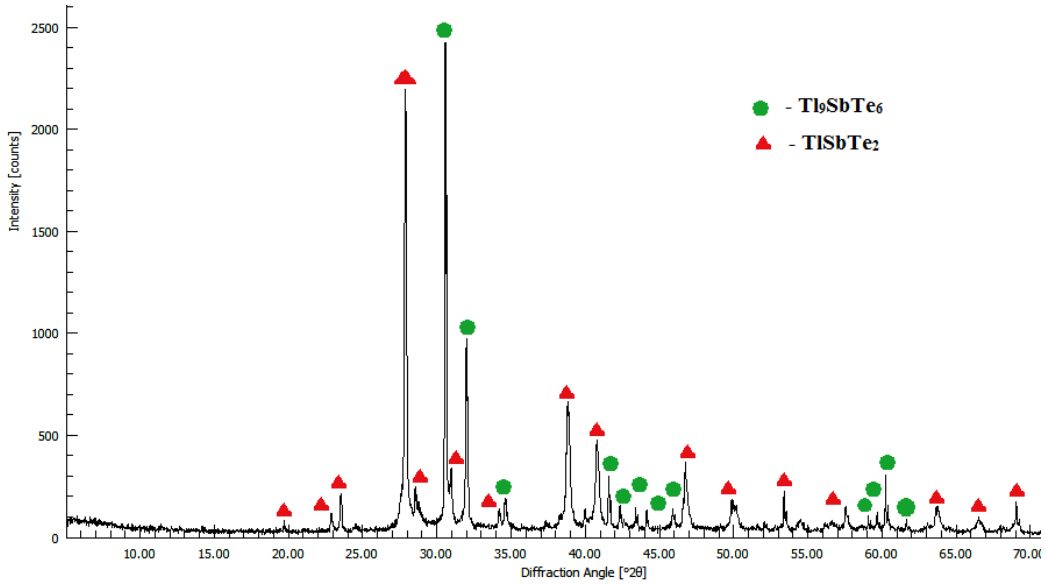
The PXRD (Bruker D8 diffractometer, CuK_α radiation) was used to control the purity of the synthesized compounds and intermediate samples. The analysis was carried out at room temperature between $10° \leq 2\theta \leq 70°$. The lattice constants were calculated by indexing of powder patterns using Topas V3.0 software.

DTA was performed using a NETZSCH 404 F1 Pegasus differential scanning calorimeter. The analysis was carried out within room temperature and ~1400 K depending on the composition of the alloys at a heating rate of 10 K· min^{-1}. Temperatures of thermal effects were taken mainly from the heating curves.

3. Results and discussion

The Tl_9TbTe_6-Tl_9SbTe_6 section divides the Tl_2Te-$TlTbTe_2$-$TlSbTe_2$ into 2 subsystems: Tl_2Te-Tl_9TbTe_6-Tl_9SbTe_6 and Tl_9SbTe_6-Tl_9TbTe_6 -$TlTbTe_2$-$TlSbTe_2$. The first one studied by authors of (Imamaliyeva *et al*., 2018a).

In order to determine the character of the solid-phase equilibria in the $TlTbTe_2$-Tl_9TbTe_6-Tl_9SbTe_6-$TlSbTe_2$ sub-system, we studied a series of equilibrium alloys from this region by the XRD method. It was found that the interaction of the δ-phase (continuous solid solutions in the Tl_9SbTe_6-Tl_9TbTe_6 system) with solid solutions based on $TlTbTe_2$ (β_1) and $TlSbTe_2$ (β_2) leads to the formation of wide two-phase (β_1+δ and β_2+δ) fields separated by a β_1+β_2+ δ three-phase area. As a sample, Fig. 1 shows powder XRD patterns from β_1+δ two-phase (# 1) and β_1+β_2+δ three-phase (# 2) regions.



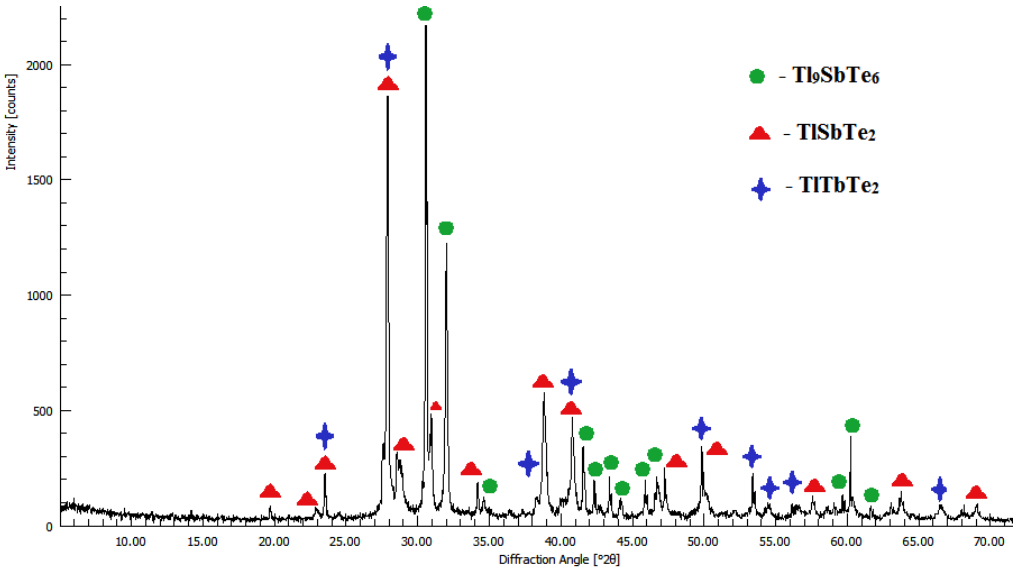


Figure 1. The powder XRD patterns from two- (samples #1) and three-phase (samples #2) areas of the Tl_9SbTe_6-Tl_9TbTe_6 -$TlTbTe_2$-$TlSbTe_2$ subsystem

The following crystal lattice parameters were obtained based on the indication of the powder XRD patterns of the samples # 1 and # 2:

Sample #1: a=4.4181, c=23.998 (β_2-phase); a=8.8507, c=12.986 Å (δ-phase)

Sample #2: a=4.4237, c=23.375 (β_1-phase); a=4.4182, c=23.996 Å (β_2-phase); a=8.8506, c=12.985 Å (δ-phase).

A comparison of these data with the results of (Imamaliyeva *et al*., 2018a; Alakbarzade, 2019) shows that sample #1 consist of two-phase mixture of β_2-phase with composition ~70 mol% $TlSbTe_2$ along the section $TlTbTe_2$-TlSbTe (Table 1) and δ-phase with composition 50 mol% Tl_9SbTe_6 along the section Tl_9TbTe_6-Tl_9SbTe_6. Sample #2 consist of three-phase mixture $\beta_1+\beta_2+\delta$ with the following phase compositions: β_1 and β_2 - 10 and 70 mol% $TlSbTe_2$ along the section $TlTbTe_2$- $TlSbTe_2$ (Table 1), and δ- 50 mol% Tl_9SbTe_6.

Thus, according to the XRD data, in the three-phase region $\beta_1+\beta_2+\delta$, the compositions of the coexisting phases are 10 mol% $TlSbTe_2$ (β_1), 70 mol% $TlSbTe_2$ (β_2) and 50 mol% Tl_9SbTe_6 (δ). It should be noted that the lattice parameters of the β_2 phase in both samples are almost identical. This indicates that the composition of the sample #1 is located on the $\beta_2+\delta$ tie-line with a limiting composition of β_2 phase (Fig. 1).

Based on these data, we constructed a solid-state equilibria diagram of the Tl_9SbTe_6-Tl_9TbTe_6 -$TlTbTe_2$-$TlSbTe_2$ subsystem (Fig.2).

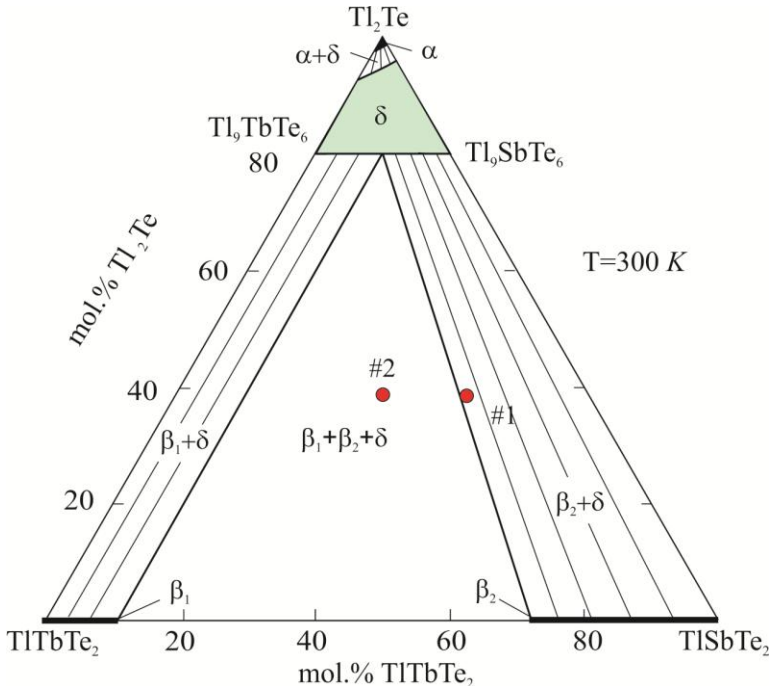


Figure 2. The solid-phase equilibria diagram of the Tl_2Te-$TlTbTe_2$-$TlSbTe_2$ system

4. Conclusion

The scheme of the solid-phase relations in the Tl_2Te-$TlSbTe_2$-$TlTbTe_2$ system at room temperature is established based on DTA and powder XRD methods. The formation of solid solutions based on $TlTbTe_2$ (β_1-phase), $TlSbTe_2$ (β_2-phase), and δ – phase (solid solutions in the Tl_9TbTe_6-Tl_9SbTe_6 system) was found in the system. Between the above-mentioned phases, the two-phase (β_1+ δ and β_2+ δ) are formed, which are limited by β_1+β_2+ δ three-phase area. The types and lattice parameters of some samples are calculated. The obtained solid solutions β_1, β_2, and δ are of great interest as potential magnetic topological insulators and thermoelectric materials.

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