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PHYSICOCHEMICAL INTERACTIONS IN $TlBiTe_2$ -Tl_8GeTe_5 (Tl_2GeTe_2) SYSTEMS

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Abstract. $TlBiTe_2$-Tl_8GeTe_5 and $TlBiTe_2$-Tl_2GeTe_2 sections of the Tl_2Te-$GeTe$-Bi_2Te_3 quasi-ternary system were studied by DTA and XRD methods, and their *T-x* phase diagrams were constructed. Both sections were found to be stable in subsolidus and form a wide range of solid solutions based on $TlBiTe_2$ and Tl_8GeTe_5 compounds. The formation of solid solutions based on $TlBiTe_2$ is accompanied by metatectic equilibrium.

Keywords: *thallium-germanium tellurides, thallium-bismuth tellurides, phase diagram, solid solutions.*

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1. Introduction

Tellurides of heavy *p*-elements, in particular bismuth and thallium tellurides, have received great research attention for a long time as thermoelectric materials with anomalous low thermal conductivity (Abrikosov *et al.*, 1969; Ahluwalia, 2016; Shevelkov, 2008; Scheer & Schock 2011; Rowe, 2006). After the discovery of a new class of functional materials - topological insulators (TI) (Moore, 2010), it was found that many binary and ternary tellurides of *p1-p3* elements with a layered structure are 3D TIs and are extremely promising for various applications, including spintronics, quantum computing, medicine, systems security, etc. (Cava *et al.*, 2013; Holtgrewe *et al.*, 2020; Filnov *et al.*, 2020; Papagno *et al.*, 2016; Sterzi *et al.*, 2018; Hogan *et al.*, 2019). The search and development of methods for the directed synthesis of complex inorganic phases, in particular chalcogenide phases, is based on data on phase equilibria and thermodynamic properties of the corresponding systems (Babanly, 2017; 2019).

The Tl-Ge-Bi-Te system is of considerable interest in terms of the search for new multicomponent telluride phases since the known tellurides of thallium-germanium (Kulieva & Babanly 1982a; 1982b; Abba-Toure *et al.*, 1991; Kurosaki *et al.*, 2008), thallium-bismuth (Babanly *et al.*, 1985; Pradel *et al.*, 1982; Wolfing *et al.*, 2001; Kurosaki *et al.*, 2003) and germanium-bismuth (Alakbarova *et al.*, 2021, 2022; Rosenthal *et al.*, 2011; Omoto *et al.*, 2015) exhibit high thermoelectric performance. Relatively recently, it was found that the $TlBiTe_2$, $Ge_2Bi_2Te_5$, $GeBi_2Te_4$, $GeBi_4Te_7$ compounds, etc. are TIs (Okamoto *et al.*, 2012; Nurmamat *et al.*, 2020; Peng *et al.*, 2020; Sterzi *et al.*, 2018). An analysis of the literature also shows that Ge-B^V-Te alloys are widely used in optical storage devices and have recently been considered the main class of phase-change materials (Tominaga, 2018; Jones, 2020; Liu *et al.*, 2021).

On the Tl_2Te-GeTe-Bi_2Te_3 concentration plane of the above quaternary system, one can expect the formation of new phases of variable composition based on the above-mentioned ternary compounds.

In previous works, we presented phase diagrams of the Tl_8GeTe_5-Tl_9BiTe_6 (Alakbarova *et al.,* 2015), Tl_2Te-Tl_8GeTe_5-Tl_9BiTe_6 (Alakbarova *et al.*, 2017), Tl_2Te-Tl_5Te_3-Tl_8GeTe_5 (Alakbarova *et al.,* 2016), systems, in which wide regions of solid solutions with the Tl_5Te_3 structure were revealed. The results of the study of similar systems of the type Tl_2Te-$A^{IV}Te$-Bi_2Te_3 (A^{IV}-Sn, Pb) show that in the Tl_2Te-GeTe-Bi_2Te_3 system, various solid solution areas can also be identified based on other compounds. Taking into account the above, we continued the study of this system and in this work, we present new results on phase equilibria in Tl_8GeTe_5-$TlBiTe_2$ and Tl_2GeTe_2-$TlBiTe_2$ polythermal sections.

Tl_8GeTe_5 and Tl_2GeTe_2 compounds melt congruently at 753 K and 690 K with peritectic reaction (Kulieva & Babanly, 1982b). According to (Babanly *et al.*, 1985), $TlBiTe_2$ melts congruently at 850 K. In (Pradel *et al.*, 1982), it is shown that the distectic melting maximum of this compound is shifted from the stoichiometric composition, and, it undergoes a phase transition at 765 K. Low-temperature modification crystallizes in hexagonal structure (*a*=4.526; *c*=23.12 Å, *z*=3, space group $R\bar{3}m$) (Pearson, 1967). The Tl_8GeTe_5 compound crystallizes in a tetragonal structure of the Tl_5Te_3 type and has the following lattice parameters: *a*=8.918, *c*=13.055 Å, *z*=2 (Kurosaki *et al.,* 2008).

2. Experimental part

High purity elements (>99.99%, Alfa Aesar, and Sigma-Aldrich) were used to synthesize the initial ternary compounds of the studied system. Stoichiometric amounts of components were filled in quartz ampoules, sealed under a vacuum of 10^{-2} Pa, and synthesized at a temperature of 50^0 above the melting point and phase purity them were examined using DTA and XRD techniques. Alloys of both systems with various ratios were prepared using these ternary compounds. The synthesis of alloys was carried out at 850 K for 3-4 h followed by quenching in icy water. Then samples were annealed at 700 K for 1300 h to form equilibrium phases.

DTA was performed on a DSC NETZSCH 404 F1 Pegasus system and a multichannel DTA device based on a TC-08 Thermocouple Data Logger. Powder diffraction patterns were recorded on a Bruker D8 diffractometer with $CuK\alpha_1$ radiation in the angle range 2θ = 10-75°. The diffraction patterns are indexed using Match 3! Crystal Impact program.

3. Results and Discussion

Based on the DTA and XRD results of the equilibrated alloys and using literature data of the Tl_2Te-GeTe and Tl_2Te-Bi_2Te_3 systems, phase diagrams of both sections were plotted.

Tl_8GeTe_5 -$TlBiTe_2$ section. The phase diagram in Fig. 1 shows that this section is practically quasi-binary and characterized by eutectic and metatectic equilibria. We have confirmed the data (Pradel *et al.*, 1982) that the distectic melting point of $TlBiTe_2$ is slightly shifted from the stoichiometric composition. Therefore, a sample of stoichiometric composition melts not at a constant temperature, but in a narrow range

(823–830 K) of temperatures (Fig.1). Eutectic (e) has a composition of 30 mol% $TlBiTe_2$ and crystallizes at 740K. $L_e \leftrightarrow \beta + \gamma$. Here β - are solid solutions based on a low-temperature modification of $TlBiTe_2$, and γ - are solid solutions based on Tl_8GeTe_5.

By constructing a complete triangle (Fig. 1), we determined that the homogeneity areas of the γ- and β-phases at eutectic equilibrium temperature cover the compositional regions of 0-17 and 86-100 mol% $TlBiTe_2$, respectively.

The formation of solid solutions based on $TlBiTe_2$ is accompanied by a decrease in its polymorphic conversion temperature (785 K) and the formation of a metatectic equilibrium at 775 K: $\beta' \leftrightarrow L + \beta$. Here β'- is a high-temperature modification of $TlBiTe_2$. Thus, the β - phase primarily crystallizes from the liquid in the range of 30-50 mol% $TlBiTe_2$, while the β'-phase primarily crystallizes in the $TlBiTe_2$-richer side of the diagram.

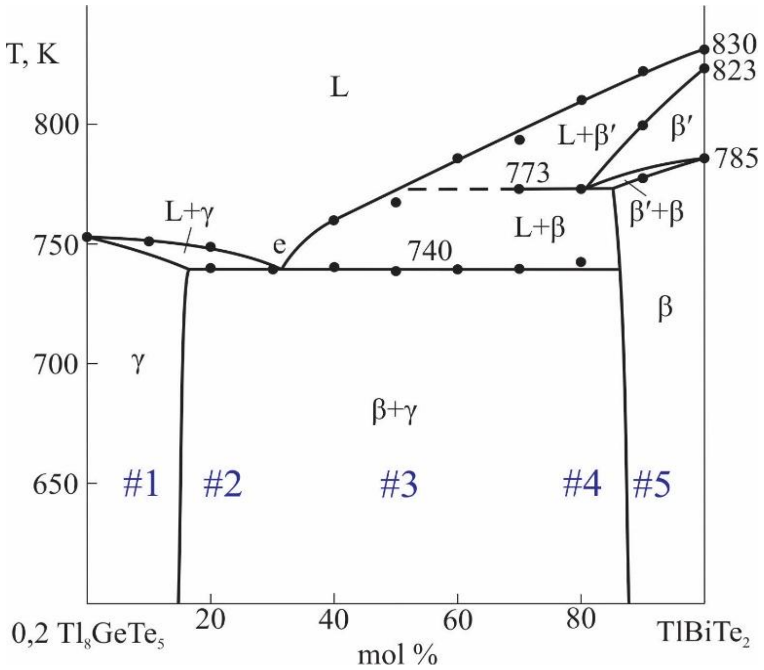

Fig. 1. Phase diagram of the Tl_8GeTe_5-$TlBiTe_2$ section

Powder diffractograms of selected samples clearly show that the Tl_8GeTe_5-$TlBiTe_2$ section is stable in subsolidus and form a wide range of solid solutions based on initial compounds (Fig. 2). As can be seen, samples containing 10 and 90 mol% $TlBiTe_2$ (# 1 and # 5 in Fig. 1) are single-phase and have diffraction patterns of Tl_8GeTe_5 and $TlBiTe_2$ compounds, respectively. Diffractograms of intermediate samples (# 2, # 3, # 4) consist of diffraction lines of β - and γ - phases.

Tl_2GeTe_2-$TlBiTe_2$ section (Fig. 3). This section is non-quasi-binary due to the incongruent melting of the Tl_2GeTe_2 compound and is stable below the solidus. Liquidus consists of 3 curves: Tl_8GeTe_5-based γ - phase primarily crystallizes from the liquid in the 0-10 mol% $TlBiTe_2$ compositional range, while the β and β' phases primarily crystallize in the compositional ranges of 10-30 and 30-100 mol% $TlBiTe_2$, respectively. The horizontal line at 750 K represents the metatectic reaction $\beta' \leftrightarrow L + \beta$.

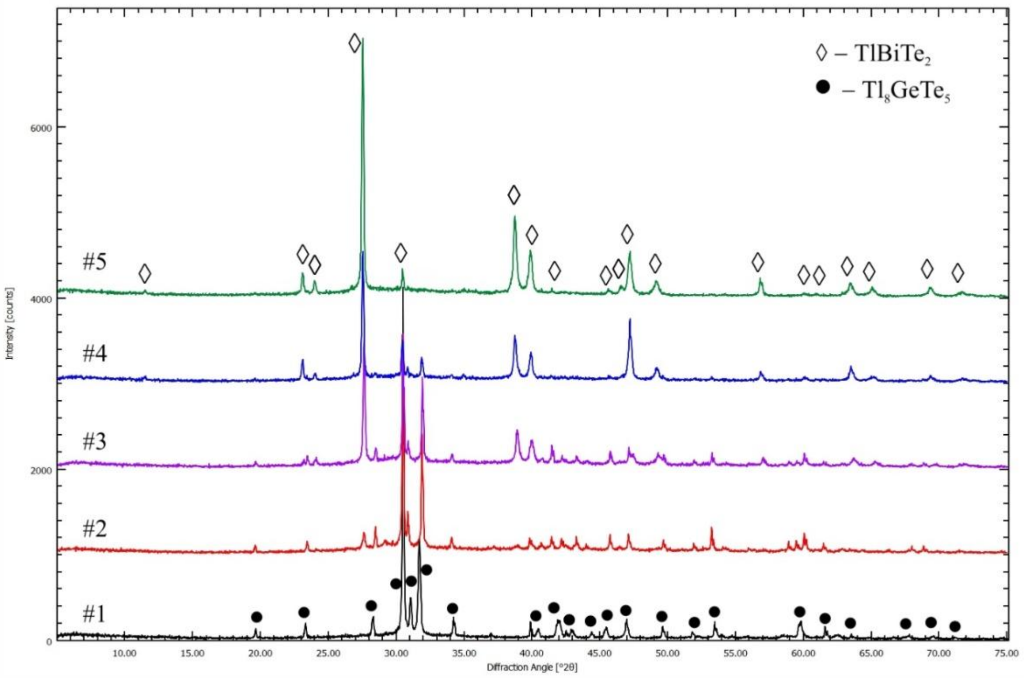

Fig. 2. XRD results of selected alloys of the Tl_8GeTe_5 -$TlBiTe_2$ section indicated in Fig. 1

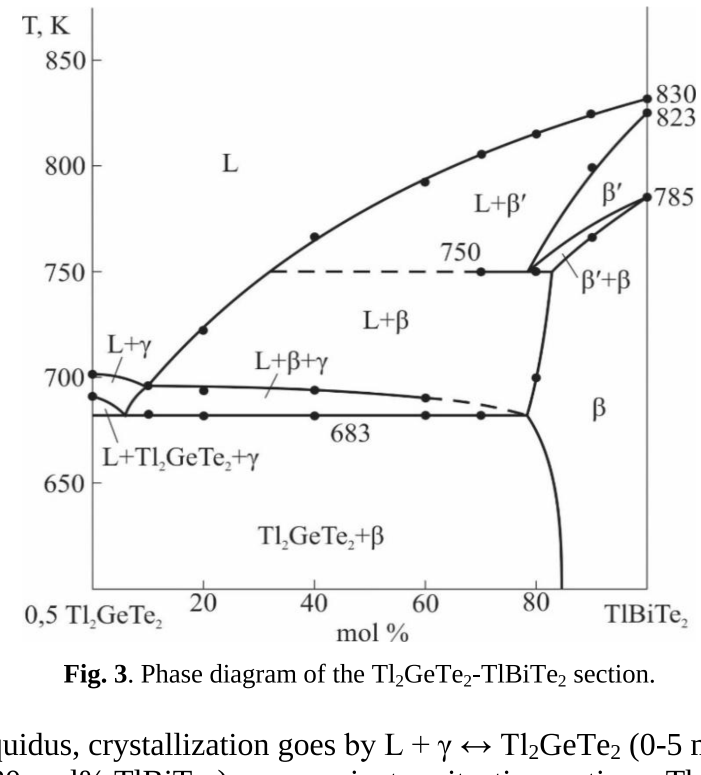

Fig. 3. Phase diagram of the Tl_2GeTe_2-$TlBiTe_2$ section.

Below the liquidus, crystallization goes by L + γ ↔ Tl_2GeTe_2 (0-5 mol% $TlBiTe_2$) and L + γ ↔ β (5-80 mol% $TlBiTe_2$) monovariant peritectic reactions. The nonvariant L + γ ↔ β + Tl_2GeTe_2 represents the completion of crystallization by the transition reaction. It can be seen from the phase diagram that there are wide solid solution areas based on both crystalline modifications of the $TlBiTe_2$ compound in this section. The XRD results for this section were also consistent with the *T-x* diagram.

4. Conclusion

In the present paper, the phase equilibria in the Tl_8GeTe_5-$TlBiTe_2$ and Tl_2GeTe_2-$TlBiTe_2$ sections of the Tl_2Te-GeTe-Bi_2Te_3 quasi-ternary system were studied for the first time. Both systems were found to be stable at subsolidus and form wide solid solution areas based on both modifications of the $TlBiTe_2$ and Tl_8GeTe_5 compounds. The constructed phase diagrams in this work and previously studied Tl_2Te-Tl_8GeTe_5-$TlBiTe_2$ subsystem allow us to determine the nature of the physicochemical interaction between thallium-germanium and thallium-bismuth tellurides.

Finally, note that the melting temperature of $TlBiTe_2$ in the *T-x* diagram of both sections (Fig. 1 and 3) is given not as a single point, but as two points covering the range 823-830 K because the distectic melting point of this compound is slightly outside the stoichiometric composition.

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