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PHASE EQUILIBRIA IN THE Tl_2Te-Tl_5Te_3-Tl_9ErTe_6 SYSTEM

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Abstract. Ternary system Tl-Er-Te was experimentally investigated in the Tl_2Te-Tl_5Te_3-Tl_9ErTe_6 compositions area by methods of differential thermal analysis, powder X-ray diffraction technique and microhardness measurements applied to equilibrated alloys. Based on the experimental data, some isopleth sections and isothermal section at 300 K, as well as projections of the liquidus and solidus surfaces, were constructed. It was shown that more than 90% of the concentration triangle is occupied by the homogeneity area of solid solutions with Tl_5Te_3 structure (δ-phase). A narrow area of solid solutions (α-phase) based on Tl_2Te was detected. α- and δ-phases are separated by α+δ two-phase area.

Keywords: *thallium-erbium tellurides, phase equilibria, solid solutions, crystal structure*.

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1. Introduction

Complex metal chalcogenides have received a lot of attention thanks to their important functional properties, such as thermoelectric, photoelectric, optical, magnetic et al. properties (Ahluwalia, 2016; Alonso-Vante, 2018; Shi *et al.*, 2019b; Kanatzidis, 2015; Sa *et al.*, 2016; Jashangeet *et al.*, 2019). In particular, some layered tellurides of p^2- and p^3- elements are topological insulators and are considered promising for use in spintronics and in topological quantum computers (Pacile *et al*., 2019; Shvets *et al.*, 2017; Papagno *et al*., 2016). Introduction to the crystal structure of d and f- elements can improve their properties and give them additional functionality, such as the magnetic properties (Viti *et al*., 2016; Aliev *et al*., 2019; Niu *et al*., 2017; Ying *et al*., 2015; Shi *et al.*, 2019a).

Owing to features of the crystal structure (Schewe *et al.*, 1989; Bhan & Shubert, 1970), thallium telluride Tl_5Te_3 is one of the most suitable matrix compounds for obtaining its new cation- and anion-substituted analogs (Babanly *et al*., 1985a,b; Imamaliyeva *et al.*, 2008; Babanly *et al*., 2005, 2015; Bratmöller & Böttcher, 1993, 1994a, b; Blachnik & Dreibach, 1984). Ternary and more complex structural analogs of Tl_5Te_3 have a number of unique functional properties, which make them quite promising for using in various modern high technologies (Piasecki *et al*., 2017; Heinke *et al*., 2017; Arpino *et al*., 2015; Bangarigadu-Sanasy *et al.*, 2014; Guo & Kleinke, 2015; Shah *et al.*, 2017; Khan *et al*., 2018).

The search and development of physico-chemical foundations of direct synthesis of new multicomponent chalcogenide phases and materials are based on knowledge on data on phase equilibria and thermodynamic properties of the corresponding systems (Tomashyk, 2016; Zlomanov, 2010). Of greatest interest are systems in which structural analogs of known binary and ternary compounds or solid solutions based on them can form (Babanly *et al*., 2017; Imamaliyeva *et al*., 2018b).

In our previous papers (Imamaliyeva *et al*., 2017, 2018a, c), we presented the results of phase equilibria investigations of a number system including Tl_5Te_3 compound or its structural analogs. We found that the former three systems are characterized by the formation of continuous solid solutions and the latter two systems-by wide areas of solid solutions.

Here we represent a detailed investigation of phase relationships of the Tl-Er-Te system in the Tl_2Te-Tl_5Te_3-Tl_9ErTe_6 composition area.

Tl_2Te and Tl_5Te_3 compounds melt congruently at 693 and 725 K and form the eutectic (695K, ~ 34 at.%Tl) (Asadov *et al.*, 1977). Tl_2Te crystallizes in the monoclinic system (space group C2/c; a = 15.662; b = 8.987; c=31.196Å, β=100.76^0, z=44) (Cerny *et al*., 2002), while tetragonal lattice parameters of Tl_5Te_3 are equal to a = 8.930; c = 12.598 Å (Schewe *et al*., 1989). Tl_9ErTe_6 melts with decomposition by the peritectic reaction at 705 K and has lattice constant: a=8.8501; c=12.9524 Å, z=2 (Mekhdiyeva *et al.*, 2018; Imamaliyeva *et al*., 2018d).

It was found that the Tl_2Te-Tl_9ErTe_6 and Tl_5Te_3-Tl_9ErTe_6 boundary systems are partially quasibinary due to the peritectic character of the melting of the Tl_9ErTe_6 compound. The former system is characterized by the formation of a wide, while the second one by continuous series of solid solutions with the Tl_5Te_3 structure based on Tl_9ErTe_6 (Imamaliyeva *et al*., 2018d).

2. Experimental

2.1. Materials and syntheses

Starting compounds Tl_2Te, Tl_5Te_3, and Tl_9ErTe_6 were synthesized by the melting of high purity elements (Table 1). Because thallium was stored in water to prevent its oxidation in air, it was dried immediately before use. Since thallium and its compounds are toxic, it was handled using protective gloves.

Synthesis of Tl_2Te and Tl_5Te_3 was carried out in evacuated (~ 10^{-2} Pa) quartz ampoules at 750 K with following slow cooling. Tl_9ErTe_6 was synthesized by alloying stoichiometric amounts of Tl_2Te, Er, and Te. This is due to Tl and Er form thermodynamically stable compounds with each other, and this somewhat complicates the synthesis of the ternary compound from elemental substances. Tl_9ErTe_6 melts incongruently (Mekhdiyeva *et al*., 2018; Imamaliyeva *et al*., 2018d). Thus and so after alloying this mixture, the obtained Tl_9ErTe_6 ingot was ground to a powder, thoroughly stirred, compacted into a pellet, and annealed at 680 K for 800 h. To prevent the interaction of quartz with erbium, the compound Tl_9ErTe_6 and alloys in the system under investigation were synthesized in graphitized ampoules.

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

All alloys of the investigated system were prepared by melting the stoichiometric quantities of the pre-synthesized binary and ternary compounds in evacuated quartz tubes at 900 K in a vertical tube furnace. After the synthesis, alloys were powdered in

an agate mortar, pressed into pellets and reheated at 680 K within 1000 h. In order to prevent a reaction between the ampoules and erbium, the quartz tubes were coated with a carbon film via the decomposition of ethanol.

Table 1. Provenance and purity of the materials used in this investigation

Chemical	Mass fraction purity	Source	CAS No	Form
Erbium	0.999	Alfa Aesar (Germany)	7440-52-0	Foil
Thallium	0.99999	Alfa Aesar (Germany)	7440-28-0	rod
Tellurium	0.9999	Alfa Aesar (Germany)	13494-80-9	broken ingots

2.2. Methods

DTA and XRD analyses, as well as microhardness measurements, were employed to analyze the samples.

DTA was performed using a NETZSCH 404 F1 Pegasus differential scanning calorimeter. The crystal structure was analyzed by a powder X-ray diffraction technique at room temperature using a Bruker D8 diffractometer utilizing CuK_α radiation within $2\theta = 10$ to $70°$. Microhardness measurements were done with a microhardness tester PMT-3, the typical loading being 20 g.

3. Results and discussion

The combined analysis of experimental and literature data on boundary systems (Asadov *et al.*, 1977; Imamaliyeva *et al.*, 2018d) enabled us to construct the self-consistent diagram of the phase equilibria in the Tl_2Te-Tl_5Te_3-Tl_9ErTe_6 system (Table 2, Fig.1-4).

Isopleth sections of the Tl_2Te-Tl_5Te_3-Tl_9ErTe_6 system (Fig.1).

Fig.1 show the isopleth sections Tl_2Te-[A] and Tl_5Te_3-[B] of the Tl_2Te-Tl_5Te_3-Tl_9ErTe_6 system, where A and B are equimolar compositions on the Tl_2Te-Tl_9ErTe_6 and Tl_5Te_3-Tl_9ErTe_6 boundary systems as shown in Fig.4.

The liquidus of Tl_2Te-[A] section consists of two curves of primary crystallization of α- and δ-phases. The intersection point of these curves corresponds to the monovariant peritectic reaction $L+\delta\leftrightarrow\alpha$ (695 K). Below the solidus, this section passes through the α, α+δ and δ phase areas.

Over the entire compositions range of the Tl_5Te_3-[B] system only δ-phase crystallizes from the melt (Fig.1a).

In order to confirm the correct construction of the Tl_2Te-[A] polythermal section in Fig. 2 the powder X-ray diffraction patterns of some alloys along this section are given.

The isothermal section of the Tl_2Te-Tl_5Te_3-Tl_9ErTe_6 system at 300 K (Fig.3) consists of three areas. Over 90% of the concentration triangle is occupied by δ-solid solutions with Tl_5Te_3 structure. α-phase based on Tl_2Te has a narrow homogeneity area in the corresponding angle of the triangle. Homogeneity areas of the α- and δ-phases are separated by α+δ two-phase region.

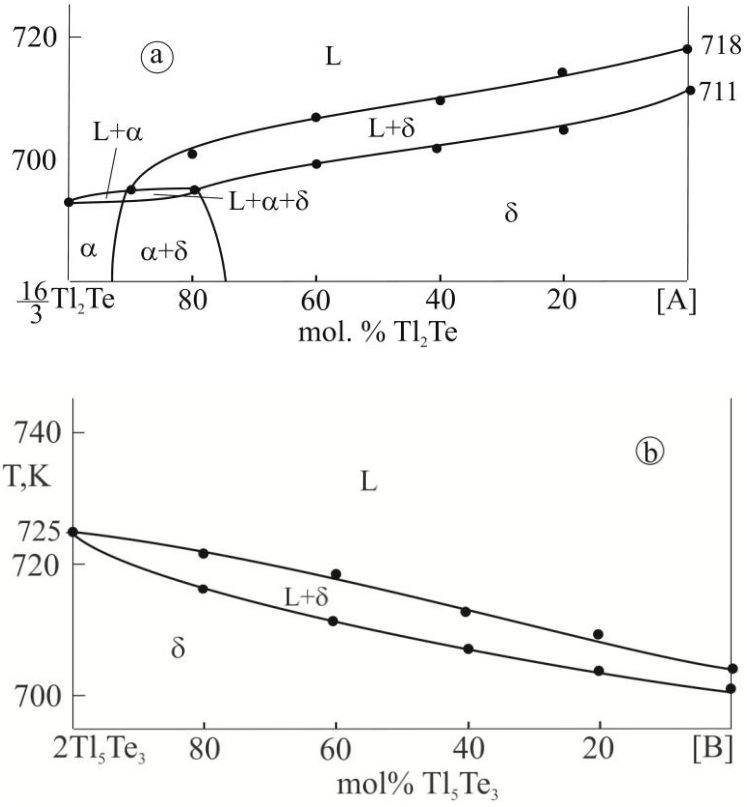

Figure 1. Isopleth sections Tl_2Te-[A] and Tl_5Te_3-[B] of the Tl_2Te-Tl_5Te_3-Tl_9ErTe_6 system

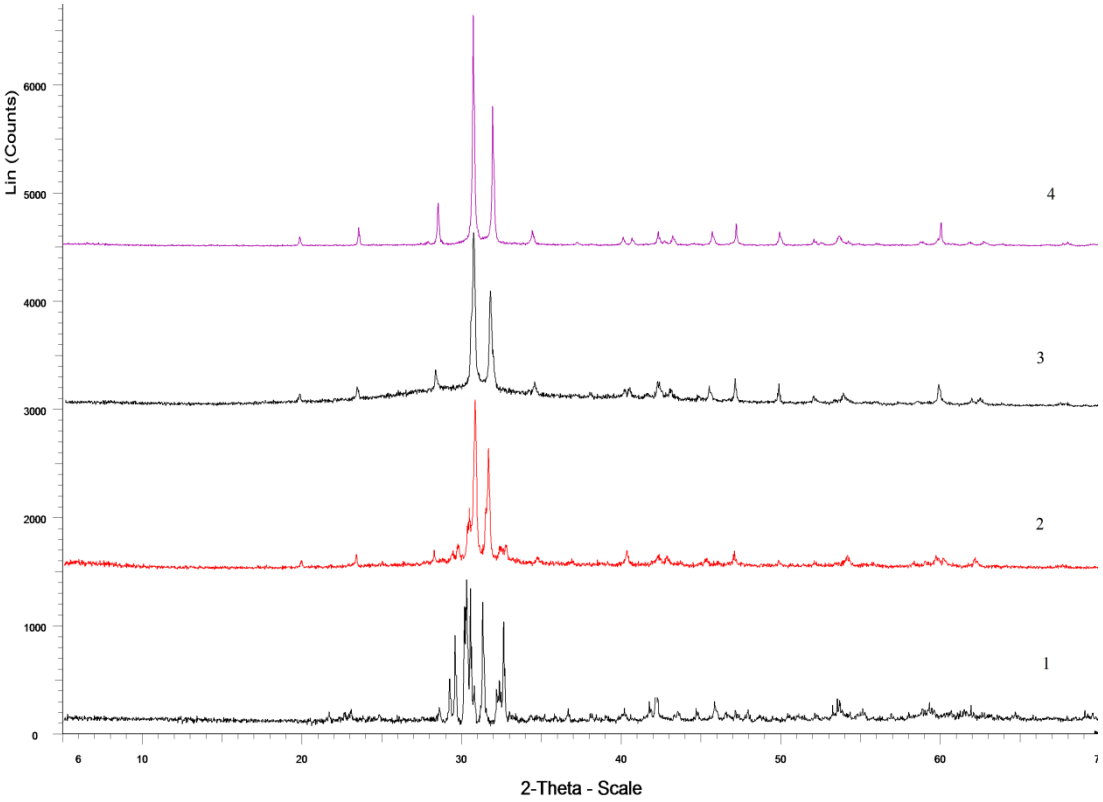

Figure 2. X-ray powder diffraction patterns of alloys of the Tl_2Te- [A] polythermal section 1- Tl_2Te; 2- 80 mol.% Tl_2Te; 3-20 mol.% Tl_2Te; 4- [A]

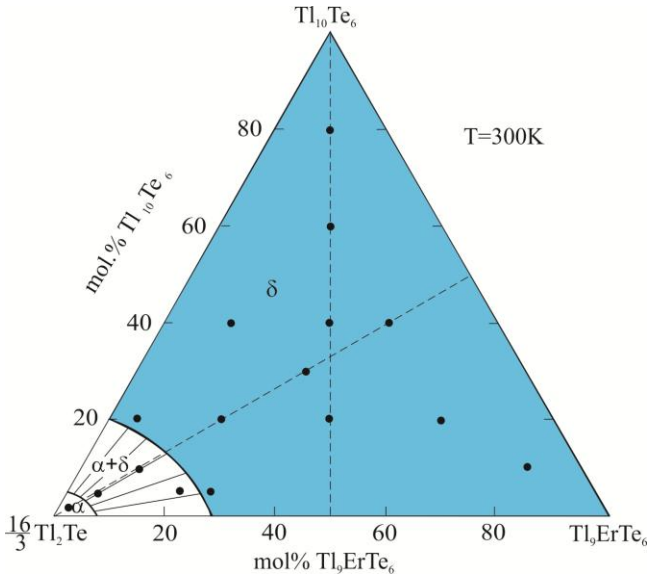

Figure 3. Isothermal section of the phase diagram of the Tl_2Te-Tl_5Te_3-Tl_9ErTe_6 system at 300 K. The circles indicate the compositions of the investigated alloys

The liquidus surface projection (Fig. 4).

Liquidus of Tl_2Te-Tl_5Te_3-Tl_9ErTe_6 system consists of three fields of the primary crystallization of α-, δ- and $TlErTe_2$ compound. These fields are separated by p_2e and p_1p_1' lines, which correspond to the monovariant peritectic equilibria L+δ↔α andL+X↔δ. Near the eutectic point (e) the peritectic equilibrium L+δ↔α must be transformed into L↔α+δ eutectic equilibrium. However, coordinates of this transformation are not experimentally fixed due to a narrow temperature range. Solidus surface consists of two areas corresponding to the completion of crystallization α- and δ-phases.

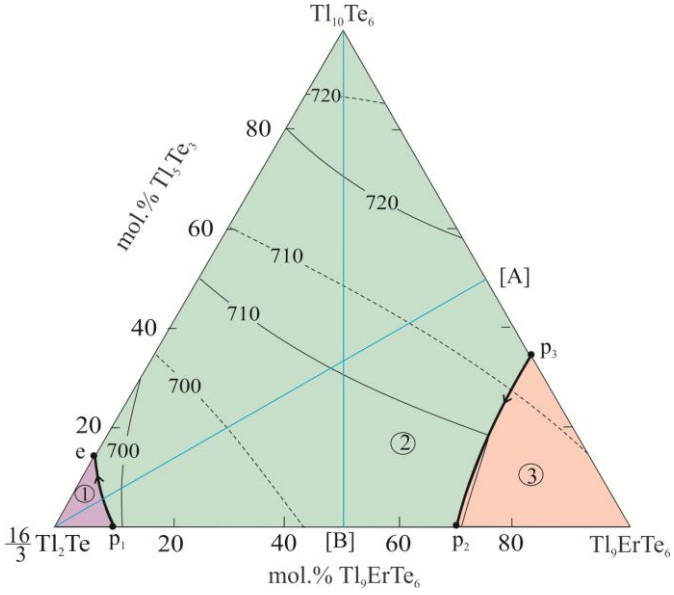

Figure 4. Projection of the liquidus and solidus (dashed lines) surface of the Tl_2Te-Tl_5Te_3-Tl_9ErTe_6 system. Primary crystallization fields of phases: 1-α; 2-δ; 3-$TlErTe_2$. Blue dash-dot lines show the investigated sections

The difference between this system and similar studied systems [Imamaliyeva,et al, 2017, 2018a, c] is the close melting points of all three initial compounds. The data presented show that on the surfaces of liquidus and solidus in this system there are no extremum points and, as a result, the temperature intervals of crystallization of the δ-phase are much narrower than in the above systems.

4. Conclusion

A full T-x-y diagram of the Tl_2Te-Tl_5Te_3-Tl_9ErTe_6 system is constructed, including some isopleth sections, an isothermal section at 300 K and liquidus and solidus surface projections. The studied system is characterized by the formation of a wide field of δ-solid solutions with the Tl_5Te_3 structure, occupying more than 90% of the concentration triangle. Obtained experimental data can be used for choosing the composition of solution-melt and for determining temperature conditions for growing crystals of δ- phase with a given composition.

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