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PHASE EQUILIBRIA ALONG THE TlTe – TlTmTe_2 AND Tl_2Te_3 – TlTmTe_2 SECTIONS OF THE Tl – Tm – Te SYSTEM**S.Z.Imamaliyeva***M.Nagiyev Institute of Catalysis and Inorganic Chemistry, NAS of Azerbaijan**samira9597a@gmail.com*

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The paper presents the results of phase equilibria studied in the TlTe – TlTmTe_2 and Tl_2Te_3 – TlTmTe_2 sections of the Tl – Tm – Te system by the methods of differential thermal and X-ray phase analyzes. T - x diagrams of both sections were constructed. It was shown that both of them are generally non-quasi-binary, but are stable below the solidus and are characterized by the connode lines between the initial compounds.

Keywords: thallium-thulium tellurides, phase equilibria, polythermal section, liquidus.

*doi***Introduction**

Chalcogenides of heavy metals possess a number of functional properties, such as photoelectric, thermoelectric, magnetic, optical other ones [1–3]. Such properties endow them various application in transistors, optoelectronics, catalysis, energy storage [4–8]. Moreover, complex thallium chalcogenides are used as topological insulators [9, 10], Weyl semimetals [11], photo-, X-ray, and gamma radiation detectors [12–14], as well as thermoelectric and magnetic materials [15–17].

Earlier, to obtain solid solutions with a Tl_5Te_3 structure, phase equilibria were studied in a number of systems consisting of Tl_5Te_3 and its ternary structural analogs [18–24].

In this work, we continued the study of phase equilibria in ternary systems based on thallium-rare earth tellurides. Previously, the ternary system Tl – Tm – Te was studied in the Tl_2Te – Tl_5Te_3 – Tl_9TmTe_6 composition [25] and along the section TlTe – Tl_9TmTe_6 [26]. It was obtained that investigated system is characterized by the formation of a wide field of δ -solid solutions with the Tl_5Te_3 structure, occupying a significant part of the concentration triangle [25]. The section TlTe – Tl_9TmTe_6 was shown to be non-quasi-binary due to the incongruent nature of the melting of both starting compounds [26].

The paper presents the results of the phase relations research in the TlTe – TlTmTe_2 and Tl_2Te_3 – TlTmTe_2 sections of the Tl – Tm – Te system.

According to [27], the TlTe and Tl_2Te_3 compounds melt incongruently at 573 and 511 K. TlTe crystallizes in tetragonal structure (Sp.Gr. $I4/mcm$, $a=12.953$, $c=6.173$, $z=16$ [28], Tl_2Te_3 – in monoclinic (Sp.Gr. Cc , $a=17.413$, $b=6.552$, $c=7.910$, $\beta=133.60$, $z=4$ [29]) and TlTmTe_2 compound have the trigonal structure of $\alpha\text{-NaFeO}_2$ -type (Sp.Gr. $R\bar{3}m$, $a=4.353$, $c=24.25$ [30].

Experimental part

Starting compounds TlTe and Tl_2Te_3 were synthesized by melting stoichiometric amounts of high purity elements in evacuated ($\sim 10^{-2}$ Pa) quartz ampoules at 600 K. TlTmTe_2 compound was synthesized by ceramic method at 1000 K. The synthesized binary compounds were annealed at 470 K for 500 h, while TlTmTe_2 was subjected to thermal annealing at 1000 K for 500 h.

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

Alloys of the investigated systems were prepared by melting the stoichiometric quantities of the initial compound in evacuated quartz tubes at 1000 K. After the fusion, the intermediate samples were powdered in an agate mortar, pressed into pellets, and annealed at 470 K within 800 h.

The investigations carried out by DTA (NETZSCH 404 F1 Pegasus differential scanning

calorimeter) from room temperature to 1350 K and powder XRD (Bruker D8 diffractometer utilizing CuK α -radiation analyses) methods.

Results and discussion

XRD of the annealed samples of the TlTe–TlTmTe₂ and Tl₂Te₃–TlTmTe₂ systems showed that they consist of two-phase mixtures of the initial compounds of investigated sections. This indicates the stability of both sections below the solidus. In Figure 1 the diffractograms of alloys with compositions 50 at.% TlTmTe₂ along both as an example, sections are cited. The reflections correspond to the reflection lines of the initial compounds without displacement, that indicates that no solid solutions in the systems.

Based on DTA using the XRD data, the T – x phase diagrams of the TlTe–TlTmTe₂ and Tl₂Te₃–TlTmTe₂ sections were plotted (Figure 2).

Both studied sections are non-quasibinary due to the incongruent melting character of initial components [25–27] (Figure 2).

TlTe–TlTmTe₂ section (Figure 2). Liquidus consists of three curves corresponding to the primary crystallization of the δ -phase, TlTmTe₂, and TmTe, which occupy 0–20, 20–35, and > 35 mol% TlTmTe₂ compositions intervals, respectively. The liquidus of the TmTe compound

has not been found experimentally, since it lies in the region of higher temperatures.

The horizontal at 1320 K corresponds to the nonvariant peritectic reaction

at 655 K – to the secondary crystallization of the δ -phase, and at 570 K – to the invariant transition reaction

In the composition interval of 5–20 mol% TlTmTe₂ and temperatures of 570–655 K, a curve with a monovariant peritectic equilibrium

is observed (Figure 2, UK curve). Near TlTe in a narrow range of compositions (0–5 mol% TlTmTe₂), the peritectic equilibrium $L + \delta \leftrightarrow \text{TlTe}$ (curve p₁U) is take place. As a result of this reaction, a three-phase region $L + \text{TlTe} + \delta$ is formed. Crystallization is completed at 570 K according to reaction (2) and the system passes into TlTe + TlTmTe₂ two-phase state.

Fig.1. Powder XRD patterns of the alloys with composition 50 mol% TlTmTe₂ along studied sections.

The Ti_2Te_3 – TiTmTe_2 section (Figure 2). Liquidus also consists of three curves corresponding to the primary crystallization of the TiTe , TiTmTe_2 , and TmTe compounds, which occupy, respectively, 0–5, 5–30, and >30 mol% TiTmTe_2 composition intervals. Part of the liquidus curve of the TmTe compound is shown by a dotted line. After the primary crystallization of TmTe , the system undergoes a peritectic reaction (1), but, in contrast to the TiTe – TiTmTe_2 section, it is monovariant along this section. There-

fore, a $\text{L}+\text{TmTe}+\text{TiTmTe}_2$ three-phase region is formed on the T – x diagram. The horizontal at 540 K corresponds to the monovariant peritectic reaction $\text{L}+\text{TiTmTe}_2 \leftrightarrow \text{TiTe}$. After this reaction, a $\text{L}+\text{TiTmTe}_2+\text{TiTe}$ three-phase region is formed in the system. Crystallization of all alloys along this section is completed at 508 K according to the transition reaction

Fig. 2. Phase diagrams of the TiTe – TiTmTe_2 and Ti_2Te_3 – TiTmTe_2 systems.

Conclusion

The Ti – Tm – Te system was studied along the TiTe – TiTmTe_2 and Ti_2Te_3 – TiTmTe_2 sections and their phase diagrams were plotted. The systems were shown to be non-quasibinary due to the incongruent character of the melting of starting compounds but stably below solidus. No new compounds and noticeable areas of solid solutions were found.

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TI–Tm–Te SİSTEMİNİN TITe–TITmTe₂ VƏ Tl₂Te₃–TITmTe₂ KƏSİKLƏRİ ÜZRƏ FAZA TARAZLIQLARI**S.Z.İmamaliyeva**

İşdə TI–Tm–Te sisteminin TITe–TITmTe₂ və Tl₂Te₃–TITmTe₂ kəsikləri üzrə faza tarazlıqlarının differensial-termiki analiz və rentgenfaza analizi üsulları ilə tədqiqinin nəticələri verilir. Hər iki kəsiyin $T-x$ diaqramı qurulmuşdur. Müəyyən edilmişdir ki, onlar bütövlükdə qeyri-kvazibinardırlar, lakin solidusdan aşağıda stabildirlər və ilkin birləşmələr arasında konnod əlaqəsi ilə səciyyələnilirlər.

Açar sözlər: tallium-tulium telluridləri, faza tarazlıqları, politermik kəsik, likvidus.

ФАЗОВЫЕ РАВНОВЕСИЯ ПО РАЗРЕЗАМ TITe–TITmTe₂ И Tl₂Te₃–TITmTe₂ СИСТЕМЫ TI–Tm–Te**С.З.Имамалиева**

Представлены результаты исследования фазовых равновесий по разрезам TITe–TITmTe₂ и Tl₂Te₃–TITmTe₂ системы TI–Tm–Te методами дифференциально-термического и рентгенфазового анализов. Построены $T-x$ диаграммы обоих разрезов. Показано, что они оба в целом неквазибинарны, но стабильны ниже солидуса и характеризуются коннодной связью между исходными соединениями.

Ключевые слова: теллуриды таллия-тулия, фазовые равновесия, политермический разрез, ликвидус.