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NEW VARIABLE COMPOSITION PHASES IN THE Tl_2Te – Tl_5Te_3 – Tl_4SmTe_3 SYSTEM

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Phase relations in the Tl–Sm–Te system were studied in the Tl_2Te – Tl_5Te_3 – Tl_4SmTe_3 composition region. The phase diagrams of boundary systems, solid-phase equilibria diagram as well as the projections of the liquidus and solidus surfaces were constructed. It was found that the homogeneity region of solid solutions with the Tl_5Te_3 structure includes the stoichiometric compositions of the compounds Tl_9SmTe_6 and Tl_4SmTe_3 , and occupies more than 90% of the area of the concentration triangle Tl_2Te – Tl_5Te_3 – Tl_4SmTe_3 . The obtained new phases are of interest as potential thermoelectric and magnetic materials.

Keywords: thallium-samarium tellurides, phase equilibria, liquidus surface, solid solutions, crystal lattice

Introduction

Chalcogenides of rare-earth elements, exhibiting unique magnetic, optical, and thermoelectric properties, are important functional materials of modern high technologies [1, 2]. The search and development of the physicochemical foundations of the directed synthesis of novel complex chalcogenide phases are based on data on phase equilibria [3, 4]. One of the advisable ways to create such materials is to search for complex structural analogs of already known compounds with the same properties and to optimize their characteristics by directed alloying [5].

One of such matrix compounds is Tl_5Te_3 [6], which, because of certain features of the crystal structure, has a number of cation-substituted structural analogs: Tl_4AX_3 , Tl_9BX_6 (A = Sn, Pb; B = Sb, Bi, Ln; X = Se, Te) [5, 7, 8]. These compounds exhibit magnetic, thermoelectric, optical, topological insulator properties [9–12].

The structural features of the Tl_5Te_3 compound and the possibility of the formation of its ternary analogs are discussed in detail in the [5]. Using the above structural features of Tl_5Te_3 , we synthesized some Tl_9LnTe_6 [5] and Tl_4LnTe_3 [13] compounds. The investigation of the phase relations in the Tl_2Te – Tl_5Te_3 – Tl_4DyTe_3 composition area of the Tl–Ln–Te system showed that the system is characterized

by the formation of a wide range of solid solutions with the Tl_5Te_3 structure [14].

In this paper, we presented the results of the investigations of phase relations in the Tl–Sm–Te system in the composition region Tl_2Te – Tl_5Te_3 – Tl_4SmTe_3 (A).

Experimental part

For the investigations, the high-purity elemental substances (Alfa Aesar) were used. The congruently melting binary compounds Tl_5Te_3 and Tl_2Te [5] were synthesized by melting stoichiometric amounts of the elemental components in evacuated (to $\sim 10^{-2}$ Pa) quartz ampules at 750 K with subsequent slow cooling.

Taking into account the previous experience [5, 13], the compounds Tl_9SmTe_6 and Tl_4SmTe_3 were synthesized by a ceramic method according to a specially developed procedure [14].

Alloys of the system (A) were also prepared by melting pre-synthesized initial compounds at 900 K in evacuated quartz ampules. Then the samples were ground into powder in an agate mortar, mixed, pressed into pellets, and annealed at 650 K for 1000 h. Initial ternary compounds and alloys of the studied system were synthesized in graphitized ampules to prevent the interaction of the samarium with the quartz ampule.

The investigations were performed by differential thermal analysis (Netzsch 404 F1 Pegasus differential scanning calorimeter) and X-ray powder diffraction (Bruker D8 diffractometer, $\text{CuK}\alpha_1$ radiation). The patterns were indexed and the lattice parameters were refined using the Topas 4.2 software by the Le Bail method.

Results and discussion

Joint processing of the experimental data allowed obtaining a complex of self-consistent data on phase relations in the system (A) (Fig.1-4, Table). Fig. 1 presents the X-ray powder diffraction patterns of some alloys in the sections Tl_5Te_3 – Tl_4SmTe_3 , Tl_2Te – Tl_9SmTe_6 , and Tl_2Te – Tl_4SmTe_3 . It is seen that, in the Tl_5Te_3 – Tl_4SmTe_3 section (Fig. 1), the initial compounds and intermediate alloys have identical X-ray powder diffraction patterns with a certain shift of reflection lines, which shows the formation of an unlimited series of solid solutions.

In the Tl_2Te – Tl_9SmTe_6 and Tl_2Te – Tl_4SmTe_3 sections, the alloys containing more than 30 mol % Tl_9SmTe_6 are single-phase, and the alloys containing 20 mol % Tl_9SmTe_6 (Tl_4SmTe_3) consist of an $\alpha + \delta$ two-phase mixture (Fig. 1).

We also studied a number of alloys outside the pointed sections, and based on the powder X-ray diffraction data, the diagram of solid-phase equilibria at 300 K was plotted (Fig.2). The subsystem (A) consists of α -, δ -phases and $\alpha + \delta$ two-phase area. The unlimited δ -solid solutions in the Tl_5Te_3 – Tl_4SmTe_3 boundary system penetrates deep into the concentration triangle and covers more than 90% of its area. A narrow homogeneity region based on Tl_2Te (α -phase) forms. These single-phase areas are limited by $\alpha + \delta$ two-phase field. Thus, the investigated concentration area of the Tl – Sm – Te ternary system below the solidus is an independent subsystem.

The section Tl_2Te – Tl_4SmTe_3 (Fig. 3) is a part of the quasi-binary system Tl_2Te – SmTe and is characterized by the formation of α - and δ -solid solutions by peritectic reactions at 707 and 772 K. The peritectic points p1 and p2 have the compositions 10 and 40 mol% Tl_4SmTe_3 , respectively. Liquidus corresponds to three curves of primary crystallization of the α - and δ -phases, as well as the SmTe compound.

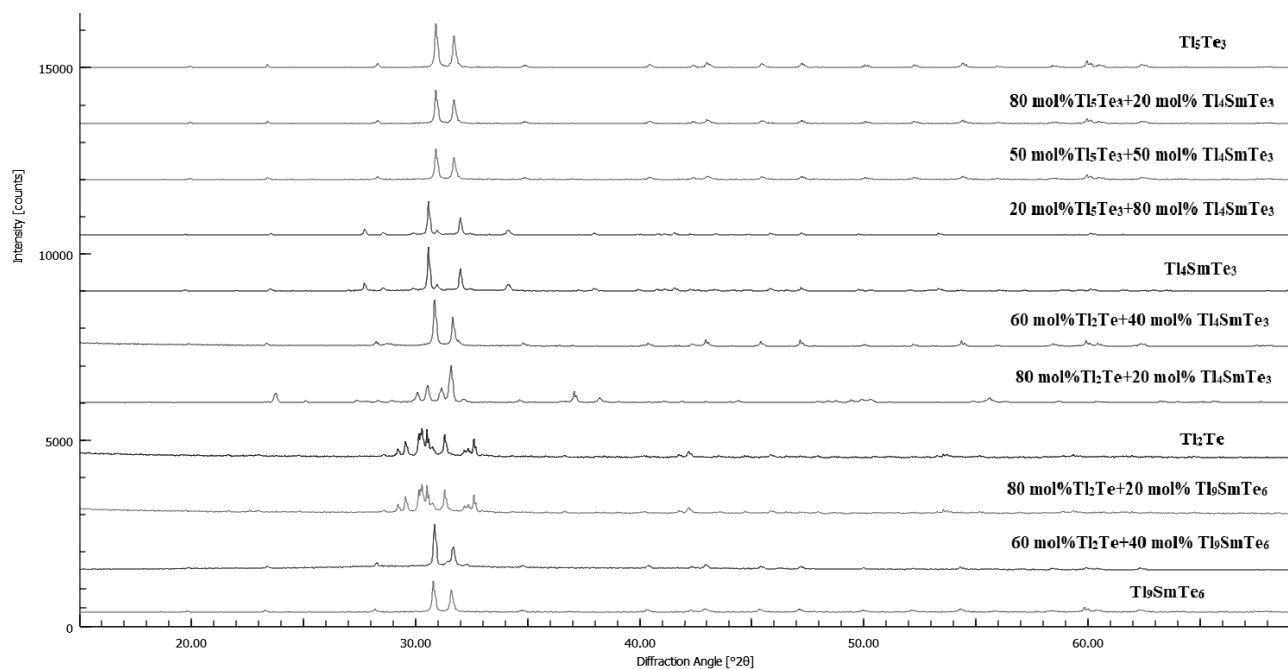


Fig. 1. X-ray powder diffraction patterns of alloys in the sections Tl_5Te_3 – Tl_4SmTe_3 , Tl_2Te – Tl_4SmTe_3 , and Tl_2Te – Tl_9SmTe_6 of the system (A)

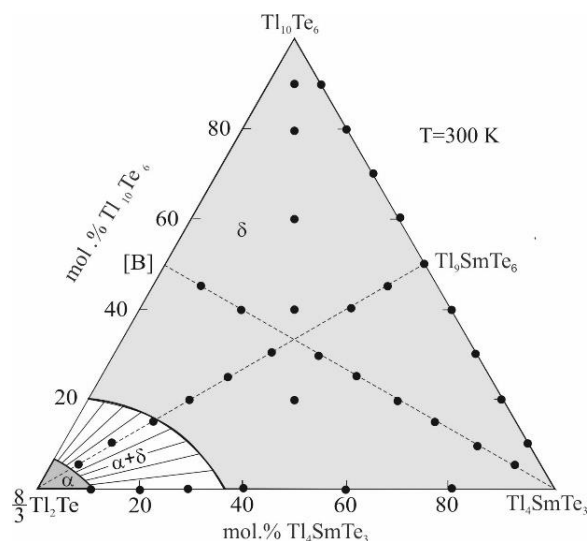


Fig. 2. Isothermal section of the phase diagram of the system (A) at 300 K

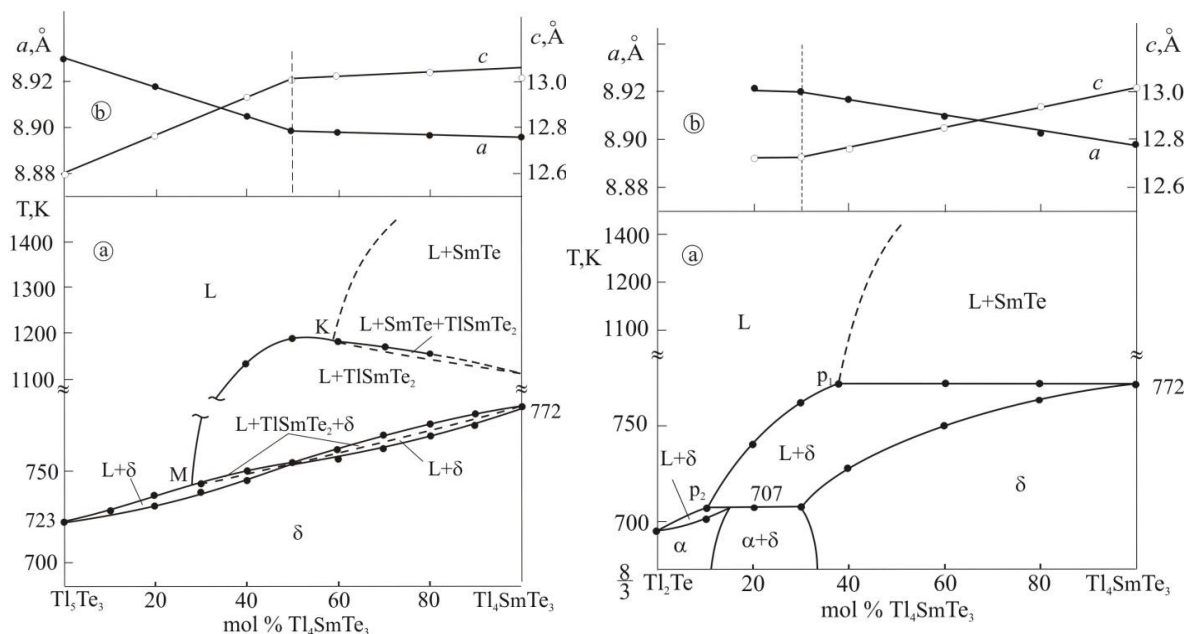


Fig. 3. Phase diagrams of the Tl_2Te - Tl_4SmTe_3 and Tl_5Te_3 - Tl_4SmTe_3 systems

The boundary system Tl_5Te_3 - Tl_4SmTe_3 (Fig. 3) is interesting in the context of the formation of unlimited solid solutions (δ -phase) with the Tl_5Te_3 structure and in the context of the fact that the ternary compound Tl_9SmTe_6 —the second structural analog of Tl_5Te_3 —is within the homogeneity region of the δ -phase. The liquidus corresponds to the primary crystallization curves of the δ -phase, TlSmTe_2 , and SmTe .

The differential thermal analysis curves show no thermal events corresponding to the liquidus of SmTe . The region $\text{L} + \text{SmTe}$ is separated by a dashed line according to Fig. 3. The dashed line also limits the three-phase region $\text{L} + \text{SmTe} + \text{TlSmTe}_2$, which separates two two-phase areas (Fig. 3). Analysis of the differential thermal analysis curves of the annealed alloys demonstrated that, unlike the other composi-

ons of the δ -phase, melting in a temperature range, the alloy containing 50 mol % Tl_4SmTe_3 (composition Tl_9SmTe_6) melts with decomposition at a constant temperature (755 K). On the other side, the concentration dependence of the parameters of the tetragonal lattice of the δ -phase clearly shows kinks at this composition. In the composition range 0-50 mol % Tl_4SmTe_3 , parameter a abruptly decreases, and parameter c increases.

Liquidus and solidus projections

The liquidus of the studied system (Fig.4) consists of 4 primary phase crystallization of the α - and δ -phases, as well as TlSmTe_2 and SmTe compounds, which exist outside the considered concentration region. These fields are separated by a number of monovariant equilibrium curves and invariant points. The table presents the types and temperatures of these equilibria.

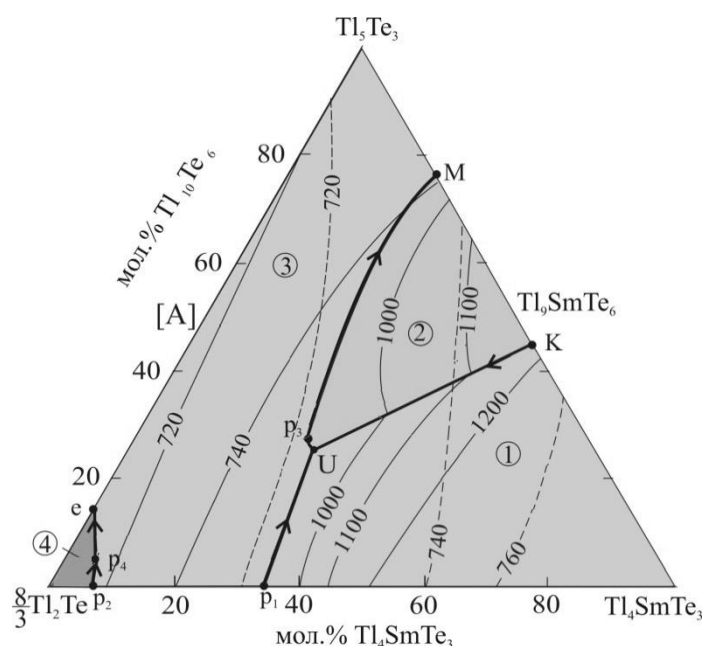


Fig. 4. Projection of the liquidus and solidus surfaces of the system (A). Primary crystallization fields: 1- SmTe , 2- TlSmTe_2 , 3 δ -, 4 α -phase. The red lines are the studied polythermal sections

Table

Non- and monovariant equilibria in the Tl_2Te - Tl_5Te_3 - Tl_4SmTe_3 system

Point or curve on the Fig.4	Equilibria	T, K
p ₁	$\text{L} + \text{SmTe} \leftrightarrow \text{Tl}_4\text{SmTe}_3$	750
p ₂	$\text{L} + \delta \leftrightarrow \alpha$	707
p ₃	$\text{L} + \text{TlSmTe}_2 \leftrightarrow \text{Tl}_9\text{SmTe}_6$	755
p ₄	$\text{L} + \delta \leftrightarrow \alpha$	703
E	$\text{L} \leftrightarrow \alpha + \delta$	693
U	$\text{L} + \text{SmTe} \leftrightarrow \text{TlSmTe}_2 + \delta$	745
KU	$\text{L} \leftrightarrow \text{SmTe} + \text{TlSmTe}_2$	1170-745
p ₂ p ₄ ; p ₄ e	$\text{L} + \delta \leftrightarrow \alpha$	707-703; 703-693
p ₁ U	$\text{L} + \text{SmTe} \leftrightarrow \delta$	750-745
Up ₃ ; p ₃ M	$\text{L} + \text{TlSmTe}_2 \leftrightarrow \delta$	750-755; 755-735

The curve KU separating the liquidus surfaces of TlSmTe_2 and SmTe is a fragment of the eutectic curve originating at the point of the invariant transition equilibrium $\text{L} + \text{Sm}_2\text{Te}_3 \leftrightarrow \text{TlSmTe}_2 + \text{SmTe}$, which is outside this concentration triangle. The interaction of the curve KU with the peritectic curve p1U leads to the establishment of the invariant transition equilibrium U in the system (Fig.4; Table). Another peritectic curve separates the liquidus surfaces of TlSmTe_2 and the δ -phase. Figure 4 shows a p3M fragment of this curve, which then goes beyond the concentration triangle of the system (A).

Conclusion

A scheme of the phase equilibria of the Tl-Sm-Te system in the $\text{Tl}_2\text{Te-Tl}_5\text{Te}_3\text{-Tl}_4\text{SmTe}_3$ composition area is presented. The phase diagrams of the boundary constituents $\text{Tl}_5\text{Te}_3\text{-Tl}_4\text{SmTe}_3$ and $\text{Tl}_2\text{Te-Tl}_4\text{SmTe}_3$, the isothermal section of the phase diagram at 300 K, and projections of the liquidus and solidus surfaces were plotted. It was determined that the homogeneity region of solid solutions based on the Tl_5Te_3 structure includes the stoichiometric compositions of the compounds Tl_9SmTe_6 and Tl_4SmTe_3 , and occupies more than 90% of the area of the $\text{Tl}_2\text{Te-Tl}_5\text{Te}_3\text{-Tl}_4\text{SmTe}_3$ concentration triangle.

REFERENCES

1. Ahluwalia G. K. Applications of Chalcogenides: S, Se, and Te. Springer; 2016. 461 p.
2. Jha A.R. Rare Earth Materials: Properties and Applications, CRC Press, United States, 2014, 371p.
3. Babanly M.B., Chulkov E.V., Aliev Z. S. et al. Phase diagrams in materials science of topological insulators based on metal chalcogenides. // Russ. J. Inorg. Chem., 2017, v.62, № 13, p.1703.
4. Babanly M.B., Mashadiyeva L.F., Babanly D.M. et al. Some issues of complex investigation of the phase equilibria and thermodynamic properties of the ternary chalcogenid systems by the EMF method // Russ. J.Inorg.Chem., 2019, v.13, p.1649-1671
5. Imamaliyeva S.Z., Babanly D.M., Tagiev D.B., and Babanly M.B. Physicochemical Aspects of Development of Multicomponent Chalcogenide Phases Having the Tl_5Te_3 Structure: A Review. // Russ. J.Inorg. Chem., 2018, v.63, №13, p.1703.
6. Schewe I., Böttcher P., Schnering H.G. The crystal structure of Tl_5Te_3 and its relationship to the Cr_5B_3 // Z.Kristallogr., 1989, Bd188, p.287-298
7. Babanly M.B., Azizulla A., Kuliev A.A. System Tl-Sb-Te . // Russ. J.Inorg.Chem., 1985, v.30, p.1051-1059
8. Gotuk A.A., Babanly M.B. and Kuliev A.A. Phase equilibria in the Tl-Sn-Te system // Inorg. Mater., 1979, v.15, № 8, p.1356-1361
9. Isaeva A. Syntheses, crystal structure and magnetic properties of Tl_9RETe_6 (RE=Ce, Sm, Gd) // Crystals, 2020, v. 10, № 4, p.1-11.
10. Guo Q., Kleinke H. Thermoelectric properties of hot-pressed ($\text{Ln}=\text{La, Ce, Pr, Nd, Sm, Gd, Tb}$) and $\text{Tl}_{10-x}\text{La}_x\text{Te}_6$ ($0.90 < x < 1.05$). // J.Alloys Compd., 2015, v.630, p.37-42
11. Piasecki M., M.G.Brik, I.E.Barchiy et al. Band structure, electronic and optical features of $\text{Tl}_4\text{Sn}_x\text{X}_3$ ($\text{X}=\text{S, Te}$) ternary compounds for optoelectronic applications // J.Alloys Compd., 2017, v.710, p. 600-607
12. Arpino K.E., Wasser B.D., and McQueen T.M. Superconducting Dome and Crossover to an Insulating State in $[\text{Tl}_4]\text{Tl}_{1-x}\text{Sn}_x\text{Te}_3$ // APL Mat., 2015, v.3, №4, p.041507
13. Imamaliyeva S.Z. New thallium tellurides with rare earth elements// Condensed Matter and Interphases. 2020, №4, p.460-465
14. Imamaliyeva S.Z., Babanly D.M., Qasymov V.A., Babanly M.B. New thallium dysprosium tellurides and phase equilibria in the $\text{Tl}_2\text{Te-Tl}_5\text{Te}_3\text{-Tl}_4\text{DyTe}_3$ system // Russ. J.Inorg.Chem., 2021, v. 66, №4, p.558-568

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$\text{Tl}_2\text{Te-Tl}_5\text{Te}_3\text{-Tl}_4\text{SmTe}_3$ SİSTEMİNDƏ YENİ DƏYİŞƏN TƏRKİBLİ FAZALAR

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Tl-Sm-Te sisteminin $\text{Tl}_2\text{Te-Tl}_5\text{Te}_3\text{-Tl}_4\text{SmTe}_3$ tərkib sahəsində faza tarazlıqları öyrənilmişdir. Sistemin bərkfaza tarazlıqlarının diaqramı, sərhəd sistemlərinin faza diaqramları, həmçinin likvidus və solidus səthlərinin proyeksiyaları qurulmuşdur. Müəyyən edilmişdir ki, sistemdə Tl_5Te_3 quruluşlu geniş bərk məhlul sahəsi əmələ gəlir, onun homogenlik sahəsi üçbucağın sahəsinin 90%-dən çoxunu tutur və Tl_9SmTe_6 , Tl_4SmTe_3 birləşmələrinin stexiometrik tərkiblərini əhatə edir. Alınmış yeni fazalar potensial termoelektrik və maqnit materialları kimi maraq doğurur.

Açar sözlər: tallium-samarium telluridləri, faza tarazlıqları, likvidus səthi, bərk məhlullar, kristal qəfəs

НОВЫЕ ФАЗЫ ПЕРЕМЕННОГО СОСТАВА В СИСТЕМЕ
 $\text{Tl}_2\text{Te}-\text{Tl}_5\text{Te}_3-\text{Tl}_4\text{SmTe}_3$

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Фазовые равновесия в системе $\text{Tl}-\text{Sm}-\text{Te}$ изучены в области составов $\text{Tl}_2\text{Te}-\text{Tl}_5\text{Te}_3-\text{Tl}_4\text{SmTe}_3$. Построены фазовые диаграммы граничных систем, диаграмма твердофазных равновесий, а также проекции поверхностей ликвидуса и солидуса. Установлено, что в системе образуется широкая область твердых растворов со структурой Tl_5Te_3 , занимающая более 90% площади концентрационного треугольника и включающая стехиометрические составы соединений Tl_9SmTe_6 и Tl_4SmTe_3 . Полученные новые фазы представляют интерес как потенциальные термоэлектрические и магнитные материалы

Ключевые слова: теллуриды таллия-самария, фазовые равновесия, поверхность ликвидуса, твердые растворы, кристаллическая решетка