UDC 544.344.3:546.289'24

**MODELING THE PHASE DIAGRAM OF THE
Tl₉TbTe₆–Tl₄PbTe₃–Tl₉BiTe₆ SYSTEM****S.Z.Imamaliyeva¹, G.I.Alakbarzade², A.N.Mamedov^{1,3}, M.B.Babanly¹**¹*M.Nagiyev Institute of Catalysis and Inorganic Chemistry, NAS of Azerbaijan*²*Azerbaijan National Aerospace Agency*³*Azerbaijan Technical University**samira9597a@gmail.com*

Received 10.12.2020

Accepted 12.02.2021

The analytical multi 3D model of phase diagram of the Tl₉TbTe₆–Tl₈Pb₂Te₆–Tl₉BiTe₆ system was obtained as temperature dependence on the composition using the Multipurpose Genetic Algorithm (MGA). It was determined that the system is characterized by the formation of continuous solid solutions with tetragonal Tl₅Te₃-type structure (δ -phase). The boundaries of the uncertainty band for the liquidus and solidus surfaces of the δ -phase and the TlTbTe₂ compound are determined. The thermodynamic functions of mixing of the solid solutions depending on the composition and temperature are determined based on the model of regular solutions of non-molecular compounds. It was established that the δ -phase possess thermodynamic stability in the entire concentration interval.

Keywords: phase diagram, thallium-terbium tellurides, thallium-lead tellurides, thallium-bismuth tellurides, solid solution, Multipurpose Genetic Algorithm, 3D modeling.

doi**Introduction**

The presence of a wide range of functional properties such as electronic, thermoelectric, optical etc. in the chalcogenides of heavy elements makes them promising functional materials in numerous areas of modern technology [1–5]. Recent studies have shown that these compounds possess topological insulator (TI) properties and can be used in spintronics and quantum computers, medicine, security systems [6–8].

The introduction of heavy metal atoms, as well as d- and f-elements into the crystal lattice of these compounds, can lead to an improvement in their thermoelectric properties [9], and also give them additional functionality, for example, magnetic properties, as well as the properties of TI [10–13].

Currently, the search for novel functional materials is carried out in the direction of complicating the composition of known compounds by obtaining solid solutions, doped phases, composites, etc. [14, 15].

It is known that telluride Tl₅Te₃ exhibits thermoelectric properties [16]. Due to the peculiarities of the crystal lattice, it has many ternary

analogs of the types Tl₉AX₆ and Tl₄BX₃ (A – Sb, Bi, In, Au, rare-earth elements; B – Sn, Pb, Mo, Cu, rare-earth elements; X – Se, Te) [15, 17–23], also possessing several functional properties, namely optical [24, 25], thermoelectric [26–29], magnetic [30, 31], as well as topological insulators properties [32, 33]. In recent years, to improve thermoelectric performance, intensive work has been carried out to study solid solutions and doped phases based on these compounds [34–37].

To obtain new variable composition phases with Tl₅Te₃-structure, we studied phase relations in a some systems consisting of Tl₅Te₃ and its ternary analogs [38–40], in which continuous substitutional solid solutions were found. The constructed phase diagrams serve as the basis for choosing the composition of melts for growing single crystals of solid solutions of a given composition by the method of directional crystallization.

By the authors of [41], 3D modeling of the phase diagram of the Tl₉SmTe₆–Tl₄PbTe₃–Tl₉BiTe₆ system was carried out.

The present work is a continuation of our research on modeling complex systems. The

purpose of this work is the 3D modeling of the phase diagram of the Tl_9TbTe_6 – Tl_4PbTe_3 – Tl_9BiTe_6 system, including the boundary systems Tl_9TbTe_6 – Tl_4PbTe_3 and Tl_9TbTe_6 – Tl_9BiTe_6 , using the uncertainty principle for heterogeneous equilibria.

Objects and equations for modeling

To modeling the $\text{Tl}_9\text{TbTe}_6(1)$ – $2\text{Tl}_4\text{PbTe}_3(2)$ – $\text{Tl}_9\text{BiTe}_6(3)$ ternary system, is necessary analytical approximation of the liquidus and solidus of the boundary systems $\text{Tl}_9\text{TbTe}_6(1)$ – $2\text{Tl}_4\text{PbTe}_3(2)$ and $\text{Tl}_9\text{TbTe}_6(1)$ – $\text{Tl}_9\text{BiTe}_6(3)$. The analytical approximation of the liquidus and solidus of the $2\text{Tl}_4\text{PbTe}_3(2)$ – $\text{Tl}_9\text{BiTe}_6(3)$ system was carried out in [41]. To equalize the number of atoms in the molecules, the thallium–lead–tellurium compound was taken as a dimer $2\text{Tl}_4\text{PbTe}_3$. To modeling these systems, we used the experimental data of [38, 40]. According to the results of the indicated papers, these cross sections are characterized by the formation of continuous solid solutions (δ -phase) with the Tl_5Te_3 structure. The $\text{Tl}_9\text{TbTe}_6(1)$ – $2\text{Tl}_4\text{PbTe}_3(2)$, $\text{Tl}_9\text{TbTe}_6(1)$ – $\text{Tl}_9\text{BiTe}_6(3)$ systems are non-quasi-binary in a certain part due to the incongruent melting character of the Tl_9TbTe_6 compound. As a result, in a wide compositions interval (up to 60 mol% Tl_9TbTe_6), the TlTbTe_2 compound first crystallizes from the melt, that leads to the formation of $\text{L}+\text{TlTbTe}_2$ two- and $\text{L}+\text{TlTbTe}_2+\delta$ three-phase areas. Below the solidus, all boundary systems are quasi-binary.

For the analytical description of the liquidus and solidus of the $\text{Tl}_9\text{TbTe}_6(1)$ – $2\text{Tl}_4\text{PbTe}_3(2)$ and $\text{Tl}_9\text{TbTe}_6(1)$ – $\text{Tl}_9\text{BiTe}_6(3)$ systems, the positions of fuzzy systems for heterogeneous equilibria were used [42–44]. Due to the monotonic temperature dependence of the liquidus and solidus on the composition for the $\text{Tl}_9\text{TbTe}_6(1)$ – $2\text{Tl}_4\text{PbTe}_3(2)$ and $\text{Tl}_9\text{TbTe}_6(1)$ – $\text{Tl}_9\text{BiTe}_6(3)$ systems, the following equations are used:

$$T(\text{liquidus})=a+bx+(c\pm\Delta)x(1-x), \quad (1)$$

$$T(\text{solidus})=a+bx+(d\pm\Delta)x(1-x). \quad (2)$$

Coefficients a and b are determined based on the melting temperatures of Tl_9TbTe_6 , Tl_4PbTe_3 and Tl_9BiTe_6 . The coefficients c and d have intervals that are associated with the ex-

perimental error. For the liquidus and solidus surfaces of the ternary system $\text{Tl}_9\text{TbTe}_6(1)$ – $2\text{Tl}_4\text{PbTe}_3(2)$ – $\text{Tl}_9\text{BiTe}_6(3)$, the following equations are used:

$$T(\text{liquidus})=yT_{\text{liq}}(1-2)+(1-y)T_{\text{liq}}(1-3)+T_{\text{liq}}(2-3)y(1-y)(1-x) \quad (3)$$

$$T(\text{solidus})=yT_{\text{sol}}(1-2)+(1-y)T_{\text{sol}}(1-3)+T_{\text{sol}}(2-3)+by(1-y)(1-x)^2 \quad (4)$$

Here, the compounds are designated: 1 – Tl_9TbTe_6 ; 2 – $(2\text{Tl}_4\text{PbTe}_3)$; 3 – Tl_9BiTe_6 . x – is the mole fraction of the component 1 – Tl_9TbTe_6 , $y = x_2/(1-x)$; $(1-y)=x_3/(1-x)$; x_2 , x_3 – mole fraction of compounds 2 and 3.

To calculate the free energy of formation of solid solutions boundary systems, a asymmetric version of the model of regular solutions was used, which has been successfully tested in [42]:

$$\Delta G_T^0 = (a + bT)x^m(1-x)^n + RT[p x \ln x + q(1-x) \ln(1-x)] \quad (5)$$

In (5) the first term represents the enthalpy of mixing of solid solutions in an asymmetric version of the model of regular solutions. For solid solutions with unlimited solubility, the mixing parameter is $a < 0$, $b > 0$ the second term represents the configurational entropy of mixing solid solutions according to the model of non-molecular compounds [43]; p and q are represent the number of different atoms in compounds. $R=8.314 \text{ J mol}^{-1} \text{ K}^{-1}$.

Solution of phase equilibrium equations by using the MGA

Optimization of the liquidus and solidus curves was carried out according to the following scheme using the MGA multipurpose genetic algorithm [44]: initially, the search range for each parameter is determined for the MGA based on the experimental data of DTA. The MGA then changes the values of the variables depending on how well these values generate the solidus and liquidus curves, which correspond to the present experimental data, taking into account the uncertainties of the experimental solidus and liquidus curves. Fuzzy logic-weighting scheme looks at all the objective values of a particular member and changes them to

a value between 0 and 1. Zero, if the value is the worst of the population. One if it falls within the experimental uncertainty. Once the objectives have been scaled, the average is taken over all objectives and that single number is the fitness for the member in the population. Using the fuzzy logic-weighting scheme, the GA is run until all the members of the population reach a fitness of 1 or at least reach a state of equilibrium where there is no more improvement. When this state is reached, the members of the final population are used to determine the uncertainty bounds on the model parameters. The population of final parameters can then be used

to bound output of the model and show where the model is most uncertain and in need of more data. The obtained analytical dependences for the liquidus and solidus of the quasibinary systems [eq.(1)–(4)] are shown in the captions of the Figure 1, 2. The equations are presented in the version for the computer. Based on the uncertainty principle, liquiduses and soliduses are represented by bands for which the coefficients of equations 1 and 2 for the systems Tl_9TbTe_6 – $2\text{Tl}_4\text{PbTe}_3$ (Figure 1), and Tl_9TbTe_6 – Tl_9BiTe_6 (Figure 2) have the following intervals, respectively: $c = 44 \div 70$ and $d = -32 \div -56$; $c = 49 \div 62$ and $d = -34 \div -46$.

Fig. 1. Phase diagram of the Tl_9TbTe_6 – $2\text{Tl}_4\text{PbTe}_3$ system. δ – are solid solutions; symbols are experimental data [38]. The curves are described by equations: 1 – $T(\text{liq})=893-113*x+70*x*(1-x)$; 2 – $T(\text{liq})=893-113*x+60*x*(1-x)$; 3 – $T(\text{liq})=893-113*x+48*x*(1-x)$; 4 – $T(\text{sol})=893-113*x-30*x*(1-x)$; 5 – $T(\text{sol})=893-113*x-40*x*(1-x)$; 6 – $T(\text{sol})=893-113*x-50*x*(1-x)$.

Fig. 2. Phase diagram of the Tl_9TbTe_6 – Tl_9BiTe_6 system. δ – are solid solutions. In Fig. 2 symbols are experimental data [39]. The curves are described by equations: 1 – $T(\text{liq})=830-75*x+62*x*(1-x)$; 2 – $T(\text{liq})=830-75*x+56*x*(1-x)$; 3 – $T(\text{liq})=830-75*x+49*x*(1-x)$; 4 – $T(\text{sol})=830-75*x-43*x*(1-x)$; 5 – $T(\text{sol})=830-75*x-50*x*(1-x)$; 6 – $T(\text{sol})=830-75*x-57*x*(1-x)$.

In equation (5) it is necessary to determine the parameter of the intermolecular interaction a and the degree of concentration m, n . For the model of strictly regular solutions, $m=n=1$. It was found that in order to approximate the thermodynamic function of formation, an asymmetric version of the model of regular solutions should be used, according to which $m \neq n \neq 1$. To solve the equation containing two functional parameters (temperature, composition) and Gibbs' excess free energy, the Multi-purpose Genetic Algorithm was used [45]. The following conditions were used to carry out the iteration process:

$$x=0 \div 1; a < 0; b > 0; m > n > 1; 750\text{K} < T < 900.$$

As a result of the calculations analytical expressions for equation (7) were determined:

$$\Delta G(\text{kJ/mol}) = (-1640 + 2.48 * T) * x^{1.3} * (1-x)^{1.1} + 8.314 * T * (2 * x * \ln(x) + (1-x) * \ln(1-x)) \quad (6)$$

Here x – mole fraction Tl_9TbTe_6 in solid solution $(\text{Tl}_9\text{TbTe}_6)_x(\text{2Tl}_4\text{PbTe}_3)_{1-x}$.

To determine the thermodynamic stability of solid solutions (Figure 1, 2), the Lupis internal stability function [46] was used:

$$\Psi = x(1-x) \frac{d^2(\Delta G/RT)}{dx^2}. \quad (7)$$

Substituting dependence (6) into equation (7), we find that in the entire concentration range $\Psi > 0$.

Results and discussion

For 3D modeling of the liquidus and solidus surfaces of the system Tl_4PbTe_3 – Tl_9TbTe_6 – Tl_9BiTe_6 , the analytical method described in [47–49] was used. Equations (3) and (4) are obtained as:

$$T(\text{liquidus TlTbTe}_2) = (-1248 + 4673 * x - 2300 * x^2) * y + (-1248 + 4673 * x - 2300 * x^2) * (1-y) \quad (8)$$

$$T(\text{liquidus}) = y * T_{\text{liq}}(1-2) + (1-y) * T_{\text{liq}}(1-3) + a * y * (1-y) * (1-x) = (893 - 113 * x + 60 * x * (1-x)) * y + (830 - 50 * x + 56 * x * (1-x)) * (1-y) + 40 * y * (1-y) * (1-x) \quad (9)$$

$$T(\text{solidus}) = y * T_{\text{sol}}(1-2) + (1-y) * T_{\text{sol}}(1-3) + b * y * (1-y) * (1-x)^2 = (893 - 113 * x - 40 * x * (1-x)) * y + (830 - 50 * x - 40 * x * (1-x)) * (1-y) + 44 * y * (1-y) * (1-x)^2 \quad (10)$$

In equations (8)–(10) and in Figure 3: x – mol. fractions of Tl_9TbTe_6 ; x_2 and x_3 – mol. fractions of Tl_8PbTe_3 and Tl_9BiTe_6 ; $y = x_2/(1-x)$. In equation (8): $x=0.65 \div 1$; $y=0 \div 1$. In equations (9), (10): $x = 0 \div 1$; $y=0 \div 1$.

Fig.3. 3D phase diagram model Tl_9TbTe_6 – Tl_8PbTe_3 – Tl_9BiTe_6 visualized by equations (8)–(10).

From Figure 3 follows that the boundary systems of the Tl_9TbTe_6 – $2\text{Tl}_4\text{PbTe}_3$ – Tl_9BiTe_6 system in the 100÷60 mol% Tl_9TbTe_6 compositions interval are non-quasibinary due to the incongruent melting character of the Tl_9TbTe_6 compound. Therefore, in the concentration range 100–60 mol% Tl_9TbTe_6 , starting from 1190 K, the TlTbTe_2 compound crystallizes from the melt, which leads to the formation of two-L+ TlTbTe_2 and three-phase L+ TlTbTe_2 + δ fields. Below solidus, unlimited solid solutions of Tl_9TbTe_6 , $2\text{Tl}_4\text{PbTe}_3$ and Tl_9BiTe_6 compounds are formed. It was found that in the entire concentration range in the temperature range $T=300$ – 900 K, the second derivative of the integral free mixing energy is greater than zero [Eq. (6)]. Therefore, the values of the stability function [Eq. (7)] are also greater than zero ($\Psi>0$) in the entire range of concentrations, that points to the thermodynamic stability of solid solutions.

Conclusions

Using the positions of fuzzy systems, analytical models of phase diagrams of the Tl_9TbTe_6 – $\text{Tl}_8\text{Pb}_2\text{Te}_6$ and Tl_9TbTe_6 – Tl_9BiTe_6 systems were obtained as a temperature dependence on the composition. The boundaries of the uncertainty band were determined for the liquidus of crystallization of solid solutions based on initial compounds and the TlTbTe_2 compound, as well as the solidus of the δ -solid solutions in the entire concentration interval. An analytical multi-3D model of the phase diagram of the Tl_9TbTe_6 – $\text{Tl}_8\text{Pb}_2\text{Te}_6$ – Tl_9BiTe_6 system were determined and visualized for both the quasiternary and nonquasiternary high-temperature part of the TlTbTe_2 crystallization. The temperature-concentration dependences of the free energy of the formation of solid solutions are determined by the asymmetric version of the model of regular solutions and the configurational entropy of mixing non-molecular compounds. Below solidus, unlimited solid solutions of the compounds Tl_9TbTe_6 , Tl_4PbTe_3 and Tl_9BiTe_6 are formed. In the entire concentration range in the temperature range $T=300$ – 900 K, the second derivative of the integral free mixing energy is greater than zero, that indicates the thermodynamic stability of solid solutions.

Acknowledgments

This work was carried out as part of the scientific program of the international laboratory “Advanced Materials for Spintronics and Quantum Computing”, created on the basis of the Institute of Catalysis and Inorganic Chemistry of ANAS (Azerbaijan) and the International Physics Center Donostia (Spain) and partially funded by a grant EIF / MQM / Elm-Tehsil-1-2016-1(26)-71/01/4-M-33.

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МОДЕЛИРОВАНИЕ ФАЗОВОЙ ДИАГРАММЫ СИСТЕМЫ Tl₉TbTe₆-Tl₄PbTe₃-Tl₉BiTe₆

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С помощью многоцелевого генетического алгоритма получена аналитическая 3D-модель фазовой диаграммы системы Tl₉TbTe₆-Tl₄PbTe₃-Tl₉BiTe₆ в виде температурных зависимостей составов равновесных фаз. Показано, что система характеризуется образованием непрерывных твердых растворов с тетрагональной структурой типа Tl₅Te₃ (δ-фаза). Определены границы полосы неопределенности кривых ликвидуса и солидуса твердых растворов δ-фазы, а также соединения TlTbTe₂. На основе модели регулярных растворов немоллекулярных соединений определены термодинамические функции смещения твердых растворов в зависимости от состава и температуры. Установлено, что δ-фаза обладает термодинамической стабильностью во всем интервале концентраций.

Ключевые слова: фазовая диаграмма, теллуриды таллия-тербия, теллуриды таллия-свинца, теллуриды таллия-висмута, твердые растворы, многоцелевой генетический алгоритм, 3D-моделирование.

Tl₉TbTe₆-Tl₄PbTe₃-Tl₉BiTe₆ SİSTEMİNİN FAZA DİAQRAMININ MODELLEŞDİRİLMƏSİ

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Çoxfunksiyalı genetik alqoritmədən istifadə etməklə Tl₉TbTe₆-Tl₄PbTe₃-Tl₉BiTe₆ sisteminin faza diaqramının tarazlıqda olan fazaların tərkiblərinin temperatur asılılıqları şəklində analitik 3D-modelləri alınmışdır. Göstərilmişdir ki, sistem Tl₅Te₃ tipli tetraqonal quruluşlu fasiləsiz bərk məhlulların (δ-faza) əmələ gəlməsi ilə xarakterizə olunur. δ-bərk məhlulların likvidus və solidus əyriləri üçün qeyri-müəyyənlik zolağının sərhədləri müəyyən edilmişdir. Qeyri-molekulyar birləşmələrin requlyar məhlul modeli əsasında bərk məhlulların qarışma termodinamik funksiyalarının tərkib və temperaturdan asılılıqları təyin edilmişdir. Göstərilmişdir ki, δ-faza bütün qatılıq intervalında termodinamik davamlıdır.

Açar sözlər: faza diaqramı, tallium-terbium telluridləri, tallium-qurğuşun telluridləri, tallium-bismut telluridləri, bərk məhlullar, çoxfunksiyalı genetik alqoritm, 3D-modelləşmə.