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MODELING THE PHASE DIAGRAMS OF THE Tl_9SmTe_6 – Tl_4PbTe_3 AND Tl_9SmTe_6 – Tl_9BiTe_6 SYSTEMS**S.Z.Imamaliyeva¹, G.I.Alakbarzade², A.N.Mamedov^{1,3}, M.B.Babanly¹***Nagiyev Institute of Catalysis and Inorganic Chemistry, NAS of Azerbaijan*²*National Aerospace Agency of the Republic of Azerbaijan*³*Azerbaijan Technical University**samira9597a@gmail.com*

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Using the multipurpose genetic algorithm, the analytical models of phase diagrams of the Tl_9SmTe_6 – $\text{Tl}_8\text{Pb}_2\text{Te}_6$ and Tl_9SmTe_6 – Tl_9BiTe_6 systems as temperature dependencies of compositions of the equilibrium phases were obtained. The boundaries of the uncertainty band for the liquidus and solidus curves of solid solutions are determined. According to the model of regular solutions of non-molecular compounds, the thermodynamic functions of mixing solid solutions depending on the composition and temperature are determined. It was found that solid solutions based on the Tl_9SmTe_6 , $\text{Tl}_8\text{Pb}_2\text{Te}_6$ and Tl_9BiTe_6 compounds are thermodynamically stable in the whole concentration range.

Keywords: *phase diagram, thallium-samarium-tellurides, solid solutions, Multipurpose Genetic Algorithm.***doi****Introduction**

Binary and complex chalcogenides of heavy *p*-elements have a number of functional properties, such as thermoelectric, photoelectric and optical [1–3]. Moreover, the discovery of topological insulator properties in some layered chalcogenide phases makes them prospective materials for spintronics and quantum calculations [4–9]. The introduction into the crystal lattice of the atoms of magnetic elements of the above-indicated phases leads to an improvement of their functional properties and appearance magnetic properties in them [10].

Thallium subtelluride Tl_5Te_3 , which crystallizes in a tetragonal structure (Sp.Gr. *I4/mcm*), is a suitable matrix compound for the fabrication of new complex chalcogenide materials [11]. There are many ternary analogs of this compound of $\text{Tl}_4\text{A}^{\text{IV}}\text{Te}_3$ and $\text{Tl}_9\text{B}^{\text{V}}\text{Te}_6$ types (A^{IV} – Sn, Pb; B^{V} – Sb, Bi) [12–14]. These compounds and complex phases based on them also have a number of unique functional properties, which makes them promising for use in various fields of modern technology [15–20]. In [21, 22] new structural analogs of the Tl_5Te_3 compound of the Tl_9LnTe_6 type (Ln – Ce, Nd, Sm, Gd, Tb) were obtained, their melting nature and melting points, as well as crystallographic parameters, were determined. Further studies showed that these com-

pounds have thermoelectric and magnetic properties [23–25].

The development of new multi-component phases of variable compositions requires the study of phase equilibria in systems composed of structural analogs of binary and ternary compounds, since the formation of solid solutions in them is expected [12, 26].

In order to obtain new phases of variable composition with a structure of the Tl_5Te_3 type, we studied phase equilibria in a number of systems consisting of Tl_5Te_3 and its ternary analogs [27–29], in which continuous substitutional solid solutions were revealed. The constructed phase diagrams serve as the basis for choosing the composition of melts for growing single crystals of solid solutions with a given composition by directional crystallization.

The purpose of this work is the modeling of the phase diagram of the Tl_9SmTe_6 – Tl_4PbTe_3 , and Tl_9SmTe_6 – Tl_9BiTe_6 system using the uncertainty principle for heterogeneous equilibria.

Objects and equations for modeling

The experimental data of [27] we used for modeling of the Tl_9SmTe_6 (1)– $2\text{Tl}_4\text{PbTe}_3$ (2) and Tl_9SmTe_6 (1)– Tl_9BiTe_6 (3) systems. According to the results of this work these systems are characterized by the formation of conti-

nuous solid solutions (δ -phase) with the Ti_5Te_3 structure. The Ti_9SmTe_6 (1)– $2\text{Ti}_4\text{PbTe}_3$ (2), Ti_9SmTe_6 (1)– Ti_9BiTe_6 (3) systems are non-quasi-binary due to the incongruent melting character of the Ti_9SmTe_6 compound. As a result, in a wide range of concentrations (up to 60 mol% Ti_9SmTe_6), the TiSmTe_2 compound crystallizes from the melt, which leads to the formation of two- ($\text{L}+\text{TiSmTe}_2$) and three-phase ($\text{L}+\text{TiSmTe}_2+\delta$) fields.

For the analytical description of the liquidus and solidus of the Ti_9SmTe_6 (1)– $2\text{Ti}_4\text{PbTe}_3$ (2), Ti_9SmTe_6 (1)– Ti_9BiTe_6 (3) systems, the uncertainty principle for heterogeneous equilibria were used in [30–32]. Due to the monotonic dependence of the temperature of liquidus and solidus on the composition for the Ti_9SmTe_6 (1)– $2\text{Ti}_4\text{PbTe}_3$ (2) and Ti_9SmTe_6 (1)– Ti_9BiTe_6 (3) systems, the following equations were 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 Ti_9SmTe_6 , Ti_4PbTe_3 and Ti_9BiTe_6 . The coefficients c and d have intervals associated with the experimental error.

To calculate the free Gibbs energy of solid solutions formation, the regular solutions model was used, which has been successfully tested in [32]:

$$\Delta G_T^0 = (a + bT)x^m(1-x)^n + RT[p\ln x + q(1-x)\ln(1-x)]. \quad (3)$$

In equation (3), the first term represents the enthalpy of mixing of solid solutions in an asymmetric version of the regular solutions model. For solid solutions with unlimited solubility, the mixing parameter is $a < 0$, $b > 0$. The second term is the configurational entropy of formation of solid solutions from ternary compounds [33]; p and q – the number of different atoms in compounds. $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$.

For determination the coordinates of heterogeneous equilibria in the listed systems the method of the multipurpose genetic algorithm (MGA) [34] was used: the search interval for the coordinates of the phase equilibrium was chosen based on the melting temperatures of

ternary pure compounds. MGA changes the temperature ($T_i^m < T < T_j^m$) and the mole fraction of the base component x , taking into account the fact that they describe the uncertainties of the experimental DTA data. A fuzzy logic scheme considers and scales all objective values from 0 to 1. The genetic algorithm is run until all members of the population have reached 1 or reached a state in which the discrepancy does not exceed the error in determining temperatures ($T = 1 \div 5 \text{ K}$) and mol fraction ($x = 0.01 \div 0.02$). The experimental values of DTA are in the middle of the uncertainty regions of the liquidus and solidus curves of quasi-binary systems (Figure 1, 2).

The obtained analytical dependences for the liquidus and solidus of the quasi-binary system (equations 1, 2) are shown in the captions of 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 Ti_9SmTe_6 – $2\text{Ti}_4\text{PbTe}_3$ (Figure. 1) and Ti_9SmTe_6 – Ti_9BiTe_6 (Figure 2) systems have the following intervals, respectively: $c = 44 \div 70$ and $d = -52 \div -70$; $c = 39 \div 52$ and $d = -43 \div -57$.

Fig. 1. Phase diagram of the Ti_9SmTe_6 – $2\text{Ti}_4\text{PbTe}_3$ system. δ -solid solutions; symbols are experimental data [27]. The curves are described by equations: 1) $T(\text{liq}) = 893 - 138x + 70x \cdot (1-x)$, 2) $T(\text{liq}) = 893 - 138x + 56x(1-x)$, 3) $T(\text{liq}) = 893 - 138x + 44x(1-x)$, 4) $T(\text{sol}) = 893 - 138x - 52x(1-x)$, 5) $T(\text{sol}) = 893 - 138x - 62x(1-x)$, 6) $T(\text{sol}) = 893 - 138x - 70x(1-x)$.

Fig. 2. Phase diagram of the Tl_9SmTe_6 – Tl_9BiTe_6 system. δ -solid solutions. In Fig.2 symbols are experimental data [27]. The curves are described by equations: 1) $T(\text{liq})=830-75x+52x(1-x)$, 2) $T(\text{liq})=830-75x+45x(1-x)$, 3) $T(\text{liq})=830-75x+39x(1-x)$, 4) $T(\text{sol})=830-75x-43x(1-x)$, 5) $T(\text{sol})=830-75 \cdot x-50 \cdot x \cdot (1-x)$, 6) $T(\text{sol})=830-75 \cdot x-57 \cdot x \cdot (1-x)$.

Due to the presence of areas of uncertainty for liquidus and solidus, to solve the equation (3) we used an asymmetric version of the regular solutions model of non-molecular compounds [33]. A MGA was used to find the parameters of this equation [34]. The following conditions were used to carry out the iteration process:

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

As a result of the calculations an analytical expressions for equation (3) were determined:

$$\Delta G(\text{kJ/mol}) = (-1640 + 2.48T)x^{1.3} \cdot (1-x)^{1.1} + 8.314T(2x \ln(x) + (1-x) \cdot \ln(1-x)) \quad (4)$$

Here x – mole fraction Tl_9SmTe_6 in solid solution $(\text{Tl}_9\text{SmTe}_6)_x(\text{2Tl}_4\text{PbTe}_3)_{1-x}$.

To determine the thermodynamic stability of solid solutions (Figures 1, 2), the Lupis internal stability function [34] was used:

$$\psi = x(1-x) \frac{d^2(\Delta G / RT)}{dx^2}. \quad (5)$$

Taking into account relation (4) into (5), we find that in the entire concentration range $\psi > 0$.

Conclusion

By applications of MGA approach, the boundaries of the heterogeneous equilibrium of liquid–solid in the Tl_9SmTe_6 – $\text{Tl}_8\text{Pb}_2\text{Te}_6$ and

Tl_9SmTe_6 – Tl_9BiTe_6 in a wide range of temperatures 300÷1200 K have been determined. As the initial data, the melting points and thermodynamic parameters of the compounds Tl_9SmTe_6 , $\text{Tl}_8\text{Pb}_2\text{Te}_6$ and Tl_9BiTe_6 , coordinates of phase diagrams as well as the minimum number of experimental DTA measurements were used. The boundaries of the uncertainty for the liquidus and solidus determined and modeled based on the determination error of the experimental data DTA and thermodynamic functions of compounds formation Tl_9SmTe_6 , $\text{Tl}_8\text{Pb}_2\text{Te}_6$ and Tl_9BiTe_6 and intermediate alloys.

The information obtained is can be used for determine the optimal conditions for the synthesis of solid solutions in the listed systems, which are of great interest as potential magnetic topological insulators and thermoelectric materials.

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Tl_9SmTe_6 – Tl_4PbTe_3 VƏ Tl_9SmTe_6 – Tl_9BiTe_6 SİSTEMLƏRİNİN FAZA DİAQRAMLARININ MODELLƏŞDİRİLMƏSİ

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Çoxfunksiyalı genetik alqoritmədən istifadə etməklə Tl_9SmTe_6 – $Tl_8Pb_2Te_6$ və Tl_9SmTe_6 – Tl_9BiTe_6 sistemlərinin faza diaqramlarının tarazlıqda olan fazaların tərkiblərinin temperatur asılılıqları şəkilində analitik modelləri alınmışdır. Bərk məhlulların likvidus və solidus ayrılma 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, Tl_9SmTe_6 , $Tl_8Pb_2Te_6$ və Tl_9BiTe_6 birləşmələri əsasında bərk məhlullar bütün qatılıq intervalında termodinamik davamlıdırlar.

Açar sözlər: faza diaqramı, tallium-samarium telluridləri, bərk məhlullar, çoxfunksiyalı genetik alqoritm.

МОДЕЛИРОВАНИЕ ФАЗОВЫХ ДИАГРАММ СИСТЕМ Tl_9SmTe_6 – Tl_4PbTe_3 И Tl_9SmTe_6 – Tl_9BiTe_6

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С помощью многоцелевого генетического алгоритма получены аналитические модели фазовых диаграмм систем Tl_9SmTe_6 – $Tl_8Pb_2Te_6$ and Tl_9SmTe_6 – Tl_9BiTe_6 в виде температурных зависимостей составов равновесных фаз. Определены границы полос неопределенности кривых ликвидуса и солидуса твердых растворов. Согласно модели регулярных растворов немоллекулярных соединений определены термодинамические функции смешения твердых растворов в зависимости от состава и температуры. Установлено, что твердые растворы на основе соединений Tl_9SmTe_6 , $Tl_8Pb_2Te_6$ и Tl_9BiTe_6 термодинамически устойчивы во всем диапазоне концентраций.

Ключевые слова: фазовая диаграмма, теллуриды таллия–самария, твердые растворы, многоцелевой генетический алгоритм.