

UDC 546.863.22

CALCULATION AND 3D MODELING OF THE GIBBS ENERGY AND LIQUIDUS SURFACES OF THE YbTe-Sb₂Te₃-Bi₂Te₃ SYSTEM

**A.N.Mammadov, E.R.Tagiyev, Corresponding Member of ANAS M.B.Babanly,
Academician of ANAS D.B.Taghiyev**

In this work by using the liquidus equation applied to the YbTe-Sb₂Te₃-Bi₂Te₃ quasiternary system consisting of non-molecular compounds an approximation and 3D modelling of crystallization surfaces and partial excess Gibbs free energy for YbTe were carried out. The equations were solved on the basis of limited number of experimental points on the phase diagram and published data on boundary systems. The surfaces of the crystallization and partial excess free energy of YbTe were 3D visualized for high-temperature region (1000 ÷ 2000 K) of YbTe-Bi₂Te₃-Sb₂Te₃ systems in the concentrations range 0.25 ÷ 1.0 mole fraction of YbTe on sections $x_{\text{Bi}_2\text{Te}_3}/(x_{\text{Bi}_2\text{Te}_3} + x_{\text{Sb}_2\text{Te}_3}) = 0 \div 1$. The approximation, calculation and visualization of crystallization surfaces and partial excess Gibbs free energy of YbTe were performed by the program OriginLab2015 and Grafikus.ru/plot3d.

Keywords: calculation, approximation, 3D modeling, Gibbs free energy, liquidus YbTe, quasibinary and quasiternary systems

Introduction

Compounds Sb₂Te₃ and Bi₂Te₃ and phases based on them are widely used as thermoelectric materials [1,2]. They are also a topological insulators and can be used in spintronics and quantum computing [3,4]. Multi-component systems based on these compounds are of great interest due the possibility formation of new intermediate phases of variable composition having improved functional characteristics.

According to [5,6] phase diagrams of the YbTe-Sb₂Te₃ and YbTe-Bi₂Te₃ quasi-binary system relate to the eutectic type with a wide range of homogeneity based on Sb₂Te₃ (0.78 ÷ 1.0 mole fraction of Sb₂Te₃) and Bi₂Te₃ (0.85 ÷ 1.0 mole fraction of Bi₂Te₃). In both systems, most of the liquidus occupies the region of crystallization YbTe (0 ÷ 0.78 mole fraction Sb₂Te₃ and 0 ÷ 0.85 mole fraction Bi₂Te₃).

Quasiternary system YbTe-Sb₂Te₃-Bi₂Te₃ has phase diagram with monovariant eutectic equilibrium [5]. Liquidus surface consist of fields of primary crystallization of YbTe and wide continuous strip of solid solutions along the side system Sb₂Te₃-Bi₂Te₃. Experimental determination of liquidus surface of the compound YbTe is very difficult due to its high

melting (2003 K). In [5] the surface crystallization of the YbTe in the YbTe-Sb₂Te₃-Bi₂Te₃ system was determined by graphical extrapolation of experimental data from T ≤ 1200 K up to melting point of this compound. Thermodynamic functions of this quasiternary system at high temperatures have not been studied.

In this paper calculation and 3D modeling of crystallization surfaces and partial excess Gibbs free energy for YbTe in the YbTe-Sb₂Te₃-Bi₂Te₃ system were performed by using published data for the boundary systems and the limited number of data points on the phase diagram.

Thermodynamic calculations and results

For thermodynamic approximation of liquidus of boundary quasi-binary systems YbTe-Sb₂Te₃ and YbTe-Bi₂Te₃ following equation [7] is used:

$$\overline{\Delta G}_1^{\text{ex},l} = T \left(\Delta S_1^m - 19,144 \lg f(x_1^l) \right) - \Delta H_1^m \quad (1)$$

x_1^l - is mole fraction of YbTe in liquid solution;

T - is liquidus temperature of YbTe;

$T_l^m, \Delta H_l^m$ - are melting point and molar enthalpy of YbTe;

$$T_l^m = 2003 \text{ K}; \quad \Delta H_l^m = 35600 \text{ J mol}^{-1}.$$

The last value is calculated using two independent methods based on heats of melting of ytterbium and tellurium;

$\Delta S_l^m = \Delta H_l^m / T_l^m$ - is molar entropy of melting of YbTe;

$$\Delta S_l^m = 17.773 \text{ J mol}^{-1} \text{ K}^{-1};$$

$\overline{\Delta G}_l^{exs}$ - is partial molar excess free energy of YbTe (in $\text{J} \cdot \text{mol}^{-1}$), associated with the thermodynamic activity and activity coefficient on relation $\overline{\Delta G}_i^{exs} = RT \ln \gamma_i = RT \ln(a_i/x_i)$.

$f(x_l^I)$ - is function for converting the thermodynamic equations of phase equilibrium applied to the systems of non-molecular compounds [7,8]. For investigated systems:

$$f(x_l^I) = x_1(3-2x_1)(4/(5-3x_1))^2 \quad (2)$$

The values of the partial excess free energy of YbTe in YbTe–Bi₂Te₃ and YbTe–Sb₂Te₃ systems were approximated by the following polynomials, respectively:

$$\overline{\Delta G}_l^{exs} = -14252x^2 + 16720x - 2419 \quad (3)$$

$$\overline{\Delta G}_l^{exs} = -13600 + 64890x - 83500x^2 + 32390x^3 \quad (4)$$

Based on (3) and (4) we received the following relationship, which approximates the partial excess free energy of YbTe on crystallization surface of this compound in the YbTe(1)–Bi₂Te₃(2)–Sb₂Te₃(3) system:

$$\begin{aligned} \overline{\Delta G}_l^{exs} = & (-14252x^2 + 16720x - 2419)y + \\ & + (-13600 + 64890x - 83500x^2 + \\ & + 32390x^3)(1-y) + 1500x(1-x)^2y(1-y) \end{aligned} \quad (5)$$

In equation (5): $x = x_{\text{YbTe}} = 0.25 \div 1$;

$$y = x_2/(x_2 + x_3) = 0 \div 1;$$

Function $1500x(1-x)^2y(1-y)$ is determined on the basis of a limited number of data points on the phase diagram of ternary system. 3D model of the surface of the partial excess free energy of YbTe in liquid alloys saturated by this compound is shown in figure 1.

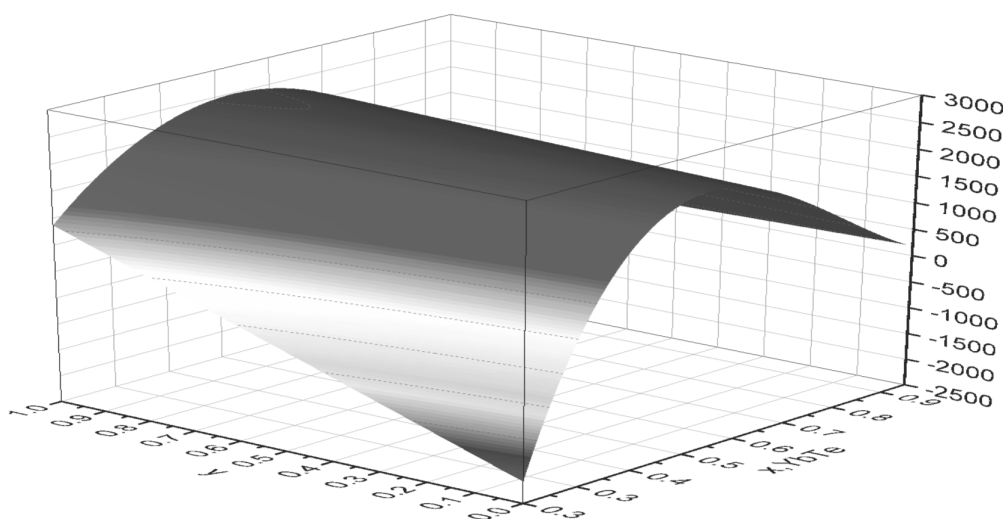


Fig. 1. 3D model of the surface of the partial excess free energy of YbTe approximated by the equation (5) for the YbTe–Bi₂Te₃–Sb₂Te₃ system

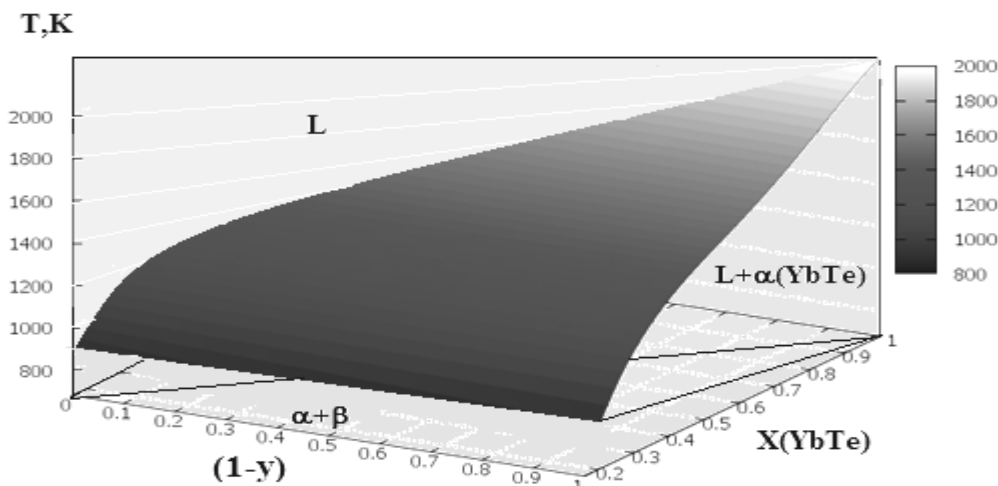


Fig. 2. 3D model of the surface crystallization of YbTe approximated by the equation (9) for the YbTe–Bi₂Te₃–Sb₂Te₃ system

From the relation (1) the following equation for calculating liquidus temperature of YbTe was received:

$$T = \frac{\Delta H_l^m + \overline{\Delta G_l^{ex,l}}}{\Delta S_l^m - 19.144 \lg f(x_l^l)} \quad (6)$$

Inserting the values of the melting enthalpy and entropy of YbTe and relations (2,5) into (6) we have got the equation for simple calculating of the liquidus temperature. This problem we decided to yet another, simpler way. The liquidus temperatures of YbTe for the binary boundary systems YbTe(1)–Bi₂Te₃(2) and YbTe(1)–Sb₂Te₃(3) were calculated according to the equation (6) and approximated by the following polynomials, respectively:

$$T_{1(1-2)} = 563 + 2260x - 1472x^2 + 653x^3 \quad (7)$$

$$T_{1(1-3)} = -322 + 8275x - 16446x^2 + 16456x^3 - 5964x^4 \quad (8)$$

Based on (7) and (8) we received the following relationship, which approximates the surface crystallization of YbTe in quasiternary system YbTe(1)–Bi₂Te₃(2)–Sb₂Te₃(3):

$$T_{1(1-2-3)} = (-322 + 8275x - 16446x^2 + 16456x^3 - 5964x^4)(1-y) + (563 + 2260x - 1472x^2 + 653x^3)y + 800x(1-x)^2y(1-y) \quad (9)$$

In equation (5): $x = x_{YbTe} = 0.25 \div 1$;
 $y = x_2 / (x_2 + x_3) = 0 \div 1$

Function $1500x(1-x)^2y(1-y)$ is defined on the basis of a limited number of experimental points on the phase diagram of ternary system. 3D model of liquidus surface YbTe approximated by the equation (9) is shown in figure 2.

Conclusion

Presented models describe the crystallization surfaces and partial excess free energy of YbTe at high temperature (1000÷2000 K) region of the YbTe–Bi₂Te₃–Sb₂Te₃ system and the concentration range 0.25÷1 mole fraction of YbTe on sections

$$x_{Bi_2Te_3} / (x_{Bi_2Te_3} + x_{Sb_2Te_3}) = 0 \div 1.$$

The dependence of the partial excess free energy of YbTe for saturated liquid alloys on composition characterized by a region of maximum. It was established, that with increasing content of Bi₂Te₃ and Sb₂Te₃, consequently, with decreasing of YbTe first increases positive deviation from ideal state. Further positive deviation is reduced when approaching 0.3 mole fraction YbTe and replaced by a negative deviation from the ideal state. This is consistent with the fact that at concentrations $x_{YbTe} = 0 \div 0.2$ in the YbTe–Bi₂Te₃–Sb₂Te₃ system formed solid solutions Sb_{2x}Bi_{2-2x}Te [5]. The obtained thermodynamic equations of approximation and 3 D models can

be used for directed synthesis of promising phases in the YbTe–Bi₂Te₃–Sb₂Te₃ system.

The work was supported by the Science Foundation of the State Oil Company of Azerbaijan Republic (Grant for the project "Preparation and investigation of new functional materials based on complex metal chalcogenides for alternative energy sources and electronic engineering", 2014).

REFERENCES

1. Шевельков А.В. Химические аспекты создания термоэлектрических материалов // Успехи химии, 2008, т.77, №1, с.3-21.
2. Тагиев Д.Б., Мамедов А.Н. Перспективные направления современной химии. Баку: Элм, 2014, 326 с.
3. Politano A., Caputo M., Nappini S., Bondino F., Aliev Z.S., Babanly M.B., Chulkov E Exploring the surface

chemical reactivity of single crystals of binary and ternary bismuth chalcogenides // J. Phys.Chem. C, 2014, v.118, p.21517-21522.

4. Okuda T., Maegawa T. Ye M., Aliev Z., Amiraslanov I., Babanly M. Experimental Evidence of Hidden Topological Surface States in PbBi₄Te₇ // Phys.Rev.Lett., 2013, v.111, p.205803-5.

5. Aliev Z.S., Rasulova K.D., Amiraslanov I.R., Tedenac J.-C., Babanly M.B. Phase diagram of the YbTe–Sb₂Te₃–Bi₂Te₃ quasi-ternary system // J.Alloys Compd., 2014, v.589, p.399–404.

6. Aliev Z.S., Ibadova G.I., Tedenac J.-C. Babanly M.B. Study of the YbTe–SnTe–Sb₂Te₃ quasi-ternary system // J.Alloys Compd., 2014, v.602, p.248–254.

7. Мамедов А.Н. Термодинамика систем с немолькулярными соединениями: расчет и аппроксимация термодинамических функций и фазовых диаграмм. LAP. Germany, 2015, 124 с.

8. Mamedov A, Mekhdiev I, Bagirov Z (1997). Thermodynamic calculation of the liquidus in ternary mutual systems // High Temperatures–High Pressures. 1997, v.29, p.689-693.

*Institute of Catalysis and Inorganic Chemistry
of ANAS
asif.mammadov.47@mail.ru*

YbTe–Sb₂Te₃–Bi₂Te₃ SİSTEMİNİN GİBBS ENERJİSİ VƏ LİKVIDUS SƏTHLƏRİNİN HESABLANMASI VƏ 3D MODELLEŞDİRİLMƏSİ

A.N.Məmmədov, E.R.Tağıyev, M.B.Babanlı, D.B.Tağıyev

İşdə likvidus tənliyini qeyri-molekulyar birləşmələrdən əmələ gəlmiş YbTe–Sb₂Te₃–Bi₂Te₃ sisteminə tətbiq etməklə YbTe-in kristallaşma və parsial izafi Gibbs enerji səthləri approksimasiya olunmuş və 3D modelləşdirilmişdir. Tənliklər sərhəd sistemlərinin ədəbiyyat məlumatları və üçlü sistemin faza diaqramındakı az sayda təcrübi qiymətləri əsasında həll edilmişdir. YbTe-in kristallaşma və parsial izafi Gibbs enerji səthlərinin YbTe–Sb₂Te₃–Bi₂Te₃ sisteminin yüksək temperatur sahəsində (1000÷2000 K), 0.25÷1.0 YbTe mol payı qatılığı və $x_{Bi_2Te_3} / (x_{Bi_2Te_3} + x_{Sb_2Te_3}) = 0 \div 1$ nəhiyələri intervallında 3D görüntüsü OriginLab2015 and Grafikus.ru/plot3d proqramları vasitəsi ilə reallaşdırılmışdır.

Açar sözlər: hesablama, approksimasiya, 3D modelləşmə, Gibbs enerjisi, itterbium-telluridin likvidusu, kvazibinar və kvaziüçlü sistemlər

РАСЧЕТ И 3D МОДЕЛИРОВАНИЕ ПОВЕРХНОСТЕЙ ЛИКВИДУСА И ЭНЕРГИИ ГИББСА СИСТЕМЫ YbTe–Sb₂Te₃– Bi₂Te₃

A.Н.Мамедов, Э.Р.Тагиев, М.Б.Бабанлы, Д.Б.Тагиев

В работе с использованием уравнения ликвидуса применительно к системе YbTe–Sb₂Te₃–Bi₂Te₃ из немолькулярных соединений проведена аппроксимация и 3D моделирование поверхностей кристаллизации и парциальной избыточной свободной энергии Гиббса для YbTe. Уравнения решены на основании литературных данных для граничных систем и ограниченного числа экспериментальных точек на фазовой диаграмме. Поверхности кристаллизации и парциальной свободной энергии YbTe 3D визуализированы для высокотемпературной области системы YbTe–Bi₂Te₃–Sb₂Te₃ в интервале температур 1000÷2000 K и концентраций 0.25÷1 моль.доли YbTe по разрезам $x_{Bi_2Te_3} / (x_{Bi_2Te_3} + x_{Sb_2Te_3}) = 0 \div 1$ с помощью программ OriginLab2015 and Grafikus.ru/plot3d.

Ключевые слова: расчет, аппроксимация, 3D моделирование, энергия Гиббса, ликвидус теллурида иттербия, квазибинарные и квазитройные системы