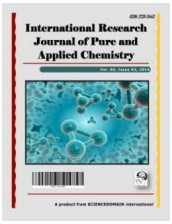

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Thermodynamic Calculation and 3d Modeling of the Liquidus Surface of the YbTe–Sb_2Te_3– Bi_2Te_3 System

A. N. Mamedov[1], E. R. Tagiev[1], L. F. Mashadiyeva[1] and M. B. Babanly[1*]

[1]Department of Functional Inorganic Materials, Institute of Catalysis and Inorganic Chemistry ANAS, H. Javid ave.113, Baku, Az1143, Azerbaijan.

Authors' contributions

This work was carried out in collaboration between all authors. Author LFM managed the literature searches. Author ANM wrote the first draft of the manuscript. Authors ANM, ERT and MBB carried out the thermodynamic calculation and 3D modeling of the liquidus and solidus surfaces. All authors read and approved the final manuscript.

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ABSTRACT

The calculation and 3D modeling of the partial Gibbs free energy and YbTe liquidus, as well as the crystallization surface of solid solutions based on $(Sb_2Te_3)_y(Bi_2Te_3)_{1-y}$ in the ternary YbTe-Sb_2Te_3-Bi_2Te_3 system were carried out by using the equations of thermodynamics of non-molecular compounds. The equations were solved on the basis of limited number of experimental points on the phase diagram and published data of boundary systems. The surfaces of the crystallization and partial excess Gibbs energy of YbTe were 3D modeled for high-temperature region (1000 - 2000 K) in the concentrations range 0.22 - 1.0 mole fraction of YbTe on sections y $=\frac{x_{Sb_2Te_3}}{1-x_{YbTe}}=$ 0-1. The calculation and modeling of Gibbs energy and crystallization surfaces was performed by the program OriginLab2015 and Grafikus.ru/plot3d.

Keywords: Thermodynamic calculation; 3D modelling; liquidus surface; YbTe-Sb_2Te_3-Bi_2Te_3 system.

**Corresponding author: E-mail: babanly_mb@rambler.ru;*

1. INTRODUCTION

Compounds Sb_2Te_3, Bi_2Te_3 and phases based on them are widely used as thermoelectric materials [1-4]. They are also topological insulators and can be used in spintronics and quantum computing [5-8]. Multi-component systems based on these compounds are very interest due the possibility of formation of new intermediate phases of variable composition having improved functional characteristics [9-12]. According to [11,12] phase diagrams of the YbTe-Sb_2Te_3 and YbTe-Bi_2Te_3 quasi-binary system have eutectic equilibria and a wide range of homogeneity based on β–Sb_2Te_3 (0.78 - 1.0 mole fraction of Sb_2Te_3) and β–Bi_2Te_3 (0.85 - 1.0 mole fraction of Bi_2Te_3). In both systems, main part of the liquidus is occupied by the region of crystallization α–YbTe (0 - 0.78 mole fractions Sb_2Te_3 and 0 - 0.85 mole fractions Bi_2Te_3). Quasiternary YbTe-Sb_2Te_3-Bi_2Te_3 system has phase diagram with monovariant eutectic equilibrium [11]. Liquidus surface consist of fields of primary crystallization of YbTe and solid solutions based on $\beta(Sb_2Te_3)_y(Bi_2Te_3)_{1-y}$. Experimental determination of liquidus surface of the compound YbTe is very difficult due to its high melting (2003 K). In [11] the crystallization surface of the YbTe in the YbTe-Sb_2Te_3-Bi_2Te_3 system is determined by graphical extrapolation of experimental data from T≤1200 K up to melting point. However thermodynamic functions of this quasiternary system at high temperatures have not been studied.

The aim of present work is calculation and 3D modeling of partial excess Gibbs energy for YbTe, crystallization surfaces of YbTe and alloys based on $(Sb_2Te_3)_y$ $(Bi_2Te_3)_{1-y}$ in the YbTe-Sb_2Te_3-Bi_2Te_3 system by using published data for the boundary systems and the limited number of experimental points on the phase diagram.

2. METHODS, RESULTS AND DISCUSSION

2.1 Thermodynamic Calculations

For thermodynamic approximation of liquidus of boundary quasi-binary systems YbTe- Sb_2Te_3 and YbTe- Bi_2Te_3 the following equation [10,13] is used:

$$\Delta\overline{G}_1^{exs,l} = T[\Delta S_1^m - 19.144\lg f(x_1^l)] - \Delta H_1^m \qquad (1)$$

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

T - is liquidus temperature of YbTe;

ΔH_1^m =35600 J·mol^{-1} – is melting molar enthalpy of YbTe, this value is calculated using two independent methods based on heats of melting of ytterbium and tellurium;

$\Delta S_1^m = \frac{\Delta H_1^m}{T_1^m}$ - is molar entropy of melting of YbTe;

ΔS_1^m =17.773 J·mol^{-1}K^{-1}; T_1^m = 2003K – is melting temperature of YbTe;

$\Delta\overline{G}_1^{exs,l}$ –is partial molar excess Gibbs energy of YbTe (in J·mol^{-1});

$f(x_1^l)$ -is function for converting the thermodynamic equations of phase equilibrium applied to the systems of non-molecular compounds [10,13-15]. For investigated systems:

$$f(x_1^l) = x_1(3-2x_1)(4/(5-3x_1)^2 \qquad (2)$$

The values of the partial excess Gibbs energy of YbTe in YbTe–Bi_2Te_3 and YbTe–Sb_2Te_3 systems were approximated by the following polynomials, respectively:

$$\Delta\overline{G}_1^{exs,l} = -14252x^2+16720x-2419 \qquad (3)$$

$$\Delta\overline{G}_1^{exs,l} = 32390x^3 - 83500x^2+64890x - 13600 \qquad (4)$$

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–Bi_2Te_3–Sb_2Te_3 system:

$$\Delta\overline{G}_1^{exs,l} = (-14252x^2 + 16720x - 2419)y + (32390x^3 - 83500x^2 + 64890x - 13600)(1-y) + 1500x(1-x)^2y(1-y) \qquad (5)$$

In equations (3-5):

$$x = x_{YbTe} = 0.25 - 1;$$

$$y = x_{Bi_2Te_3}/(1 - x_{YbTe}) = 0 - 1$$

Function $1500x(1-x)^2y(1-y)$ is determined on the basis of a limited number of experimental points on the phase diagram of ternary system [11]. 3D model of the surface of the partial excess Gibbs energy of YbTe in liquid alloys saturated by this compound is shown in Fig. 1.

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

$$T = \frac{\Delta H_1^m + \Delta \overline{G}_1^{exs,l}}{\Delta S_1^m - 19.144 lgf(x_1^l)} \quad (6)$$

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. 3D model of the liquidus surface of YbTe is shown in Fig. 2.

2.2 The Modeling of the Liquidus and Solidus Surfaces of Alloys Based on $(Sb_2Te_3)y(Bi_2Te_3)_{1-y}$

In the YbTe-Sb_2Te_3 and YbTe–Bi_2Te_3 systems there are regions of solid solutions with x_{YbTe} = 0 - 0.22 and x_{YbTe}= 0 - 0.15 mole fraction of YbTe, respectively [11,12]. In the YbTe-Sb_2Te_3-Bi_2Te_3 system there is a field of crystallization of alloys on the basis $(Sb_2Te_3)_y$ $(Bi_2Te_3)_{1-y}$ in the concentration range x_{YbTe}=0<x<0.22 and y=0 - 1. Liquidus and solidus curves in this part of the phase diagrams of YbTe-Sb_2Te_3-Bi_2Te_3 system are approximated by the following relationship:

$$T,K(liquidus)=(1326x^3-3816x^2+3774x-392)y+(-100x^2+251x+709)(1-y) \quad (7)$$

$$T,K(solidus)=(653x^2-1014x+1254)y+(400x^2-676x+1135)(1-y)-200x(1-x)^2y(1-y) \quad (8)$$

In equation (7, 8): $x = (1 - x_{YbTe}) = 0.25 - 1$; $y = x_{Sb_2Te_3}/(1 - x_{YbTe}) = 0 - 1$

Function $200x(1-x)^2y(1-y)$ is defined on the basis of a limited number of experimental points on the phase diagram of ternary YbTe-Sb_2Te_3-Bi_2Te_3 system. 3D model of liquidus and solidus surfaces of YbTe approximated by the equation (7,8) is shown in Fig. 3. Presented models describe the crystallization surfaces and partial excess free energy of YbTe at high temperature (1000-2000 K) region of the YbTe–Bi_2Te_3–Sb_2Te_3 system and the concentration range 0.25-1 mole fraction of YbTe on sections $y = x_{Sb_2Te_3}/(1 - x_{YbTe}) = 0 - 1$.

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 Bi_2Te_3 and Sb_2Te_3, 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 - 0.2 in the YbTe–Bi_2Te_3–Sb_2Te_3 system formed solid solutions on basis $(Sb_2Te_3)y$ $(Bi_2Te_3)_{1-y}$ [11].

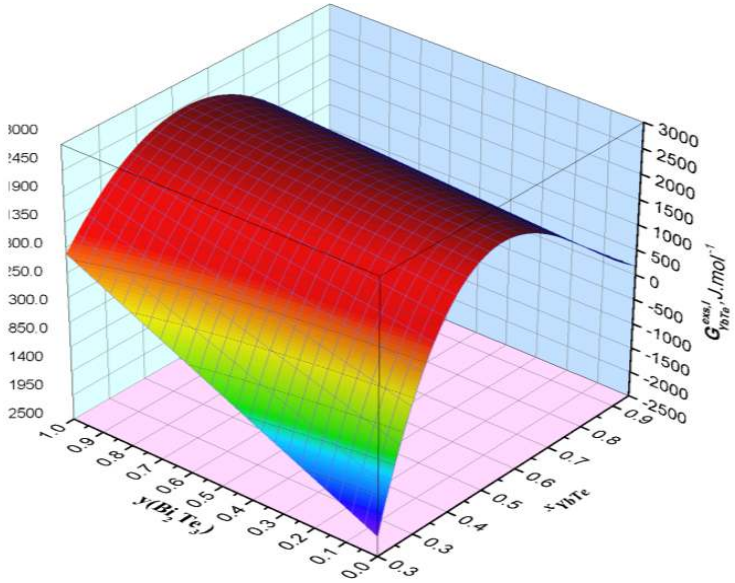

Fig. 1. 3D model of the surface of the partial excess Gibbs energy of YbTe for the YbTe–Bi_2Te_3–Sb_2Te_3 system approximated by the relationship (5)

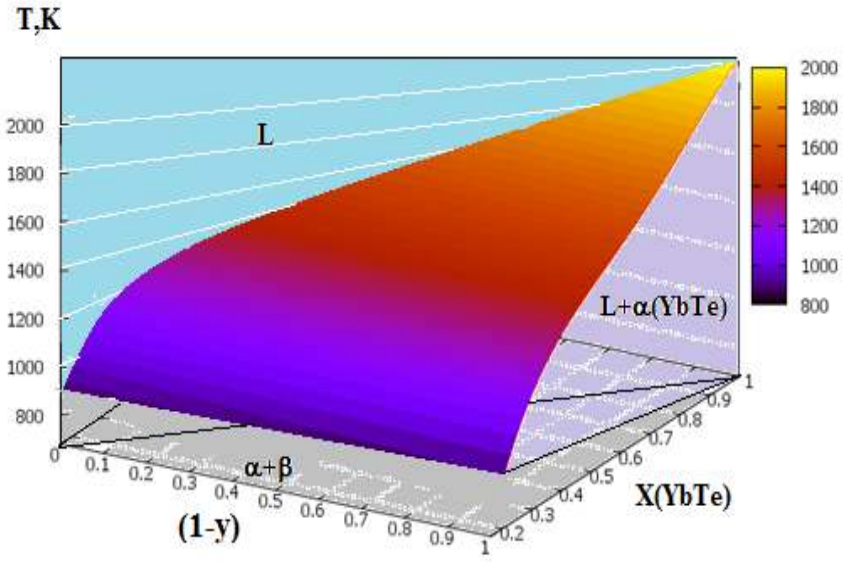

Fig. 2. 3D model of the surface crystallization of α–YbTe approximated by the equation (6) for the YbTe–Bi_2Te_3–Sb_2Te_3 system

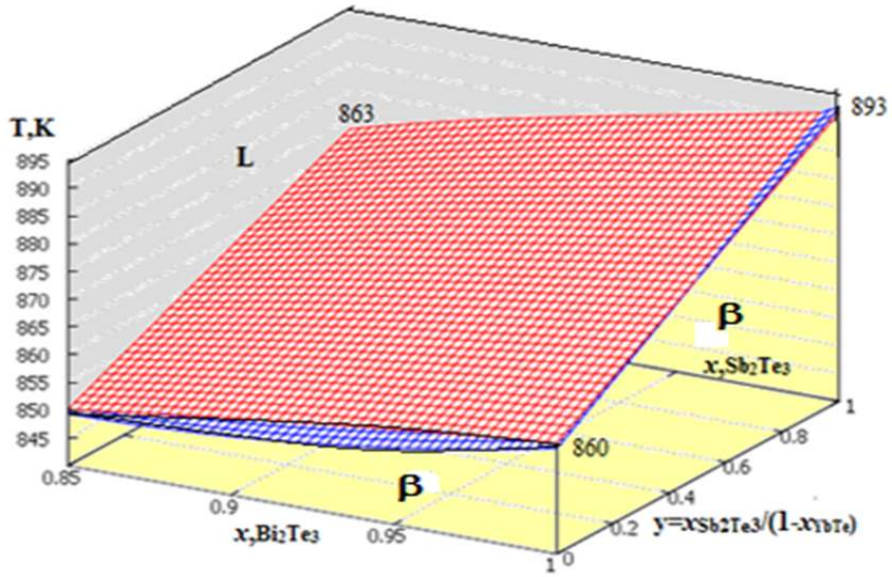

Fig. 3. 3D model of the crystallization surface of solid solutions on the basis $β(Sb_2Te_3)_y$ $(Bi_2Te_3)_{1-y}$ in the YbTe-Sb_2Te_3-Bi_2Te_3 system

3. CONCLUSION

The monovariant equilibria surface can be uniquely calculated and 3D modeled by using the equations, which are solved based on thermodynamic information obtained from the phase diagram of the binary boundary systems and a limited number of experimental data of the ternary system. The obtained thermodynamic equations of approximation and 3D models can be used for directed synthesis of promising phases in the YbTe–Bi_2Te_3–Sb_2Te_3 system.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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