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# A new thermodynamic description of the binary Bi-Te system using the associate solution and the Wagner-Schottky models

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ABSTRACT

The bismuth-tellurium system is a very important material that found application in thermoelectric devices. Interesting, the phase diagram of this system had many versions that did not agree one with another. Recently published research allowed for a precise description of phase relationship in this system; however, the proposed thermodynamic description was a simplification that not reflects physical properties of liquid phase and homogeneity range of thermoelectric phase $Bi_2Te_3$. In this work, the associate liquid solution and the Wagner-Schottky models were involved in the optimization, hence the existence of liquid clusters and homogeneity range of $Bi_2Te_3$ were reproduced.

## 1. Introduction

Thermoelectric materials are capable for a direct transformation a heat to an electricity. The thermoelectric devices have modular construction without any moving parts [1], therefore they can be applied very easy. Among many phases showing thermoelectric property, the $Bi_2Te_3$ seems to be very promising, not only because it is possible to change its characteristic from p-type to n-type, but also because of working temperature regime [2]. The efficiency of thermoelectric materials is given by a figure of merit defined as:

$$zT = \alpha^2\sigma T/\kappa \quad (1)$$

where α is a Seebeck coefficient, δ and κ are electrical and thermal conductivities, respectively, and T is an absolute temperature.

The average value of $Bi_2Te_3$ figure of merit remained around 1 for a long time [3] and this material was commercialized for using in thermoelectric refrigerators. Doping of $Bi_2Te_3$ phase by a third element, such as Se, Cu, Sb can improve the thermoelectric properties and increase a value of zT. The knowledge of phases stabilities, transformations and equilibria is crucial for doping process. All the information can be read from a phase diagram or can be calculated from a set of Gibbs energies describing the given system. In this work, a new thermodynamic description of the binary Bi-Te system is proposed. A set of consistent Gibbs energies was derived and gathered in a form of thermodynamic database. The description of each phase was chosen based on crystallographic and thermodynamic properties revealed by experiments. Proposed Gibbs energies reproduce well thermodynamic properties is essential for further interpolation to higher-ordered systems, as it was shown by Fitzner et al. [4].

## 2. Literature review

According to Mao et al. [5], the binary Bi-Te system contains seven phases: liquid, Rhombohedral_A7 (Bi), Hexagonal_A8 (Te), $Bi_2Te_3$, Beta, $Bi_2Te$, and $Bi_4Te_3$. Previous sources were inconsistent in description of phase diagram for concentration from c.a. 25 to c.a. 60 at% of Te. Hansen et al. [6] proposed one intermediate phase that was separated from terminal phases by eutectic reactions. Similarly, Brown and Lewis [7] proposed one, wide Beta phase, which homogeneity range varied from 20 to 60 at% of Te. Glazov et al. [8] suggested four intermediate phases: $Bi_7Te_3$, $Bi_2Te$, BiTe, $Bi_2Te_3$. Following Glazov et al.[8], Okamoto and Tanner [9] distinguished seven certain intermediate phases and ten uncertain linear intermetallic compounds (IMCs). Finally, Mao et al. [5] described a wide region for a concentration 25–55 at% of Te as orderly stacked units of Bi and $Bi_2Te_3$ region. Furthermore, Mao et al. [5] found two phases that are stable above a solidus of Beta-phase: $Bi_2Te$ and $Bi_4Te_3$. The liquidus line was determined by Hansen [6], Glatz [10], and Brebrick [11] by aid of differential thermal analysis (DTA). In addition, Mao et al. [5] used differential scanning calorimetry (DSC) to investigate liquidus line. The temperature of invariant reaction (Bi) + Beta = Liquid was examined by Hansen [6], Glatz [10], and Mao et al. [5]. The peritectic decomposition of Beta phase: L + $Bi_2Te_3$ = Beta was studied by Glatz [10], Brebrick [11] and Mao et al. [5]. The eutectic reaction $Bi_2Te_3$ + (Te) = Liquid was investigated by Hansen [6], Glatz [10], Brebrick, and Mao et al. [4]. Generally, all the data are self-consistent. Additionally, Mao et al. [5] studied invariant reactions

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connected to formation and decomposition of two intermetallic compounds: $Bi_2Te$ and $Bi_4Te_3$.

The homogeneity range of $Bi_2Te_3$ was determined by Brebrick [11] as a very narrow phase, where composition of Te varies between 59.7 and 60.2 at% of Te. Although the homogeneity range seems to be negligible, it is important from the view of thermoelectric property of material due to possibility of changing type of semiconducting. The homogeneity range was explained by Xu et al. [12] as anti-site defects of crystal structure of $Bi_2Te_3$ intermetallic compound. According to Kim et al. [13] excess of Te in Bi sublattice enhanced n-type of semiconducting. The p-type of semiconducting can be increased by doping by the third element, e.g. Sb [13]. The literature review does not reveal any information about charging defects in a case of $Bi_2Te_3$ IMC. The thermodynamic properties in the solid phases are limited to enthalpy of formation of $Bi_2Te_3$ phase at 298 K determined by Howlett et al. [14], Boncheva-Mladenova et al. [15], Vecher et al. [16], Wagman et al. [17], and Sidorko et al. [18]. The data is scattered and varies from -65 kJ/mol to -85 kJ/mol with experimental error +/- 10 kJ/mol. In addition, Zurhelle et al. [19] performed abinitio calculation and modeled enthalpy of formation $Bi_2Te_3$ equal -101 kJ/mol at 298 K. The heat capacity of $Bi_2Te_3$ was measured by Mills [20] at temperature range 298–850 K, and by Gorbachuk et al. [21] at temperature 80–298 K. Zurhelle at al. [19] modeled the heat capacity of $Bi_2Te_3$ based on abinitio calculations. Mixing enthalpy of liquid were measured by Maekawa et al. [22] at 877 K, Morgant et al. [23] at 863 K and 911 K and Blachnik and Enninga [24] at 873 K. All the data agree each another and show a quite sharp extremum around concentration 60 at% of tellurium. This sharp extremum point suggests a liquid associate $Bi_2Te_3$. The assumption of a liquid cluster can be confirmed in literature: Castanet and Laffitte [25] described unlike atom clusters in ternary Bi-Te-Sb liquid nearby binary Bi-Te system. Furthermore, viscosity measurements done by Kanada and Colbrun [26] and Glazov et al. [27] confirmed the liquid associate. The partial dissolution enthalpy of Bi and Te in high dilute alloys was measured by Yassin et al. [28] at 755 K.

Activity of Te in liquid alloys were determined by Predel et al. [29] by aid of vapour preassure measurement. The Knudsen effusion method was used by Belton and Fruehan [30] for measurement of elements activity in liquid Bi-Te with three different concentrations. Ohashi et al. [31], Feutelais et al. [32], and Kameda et al. [33] used electromotive force measurement for activity determination.

In addition to measurements listed above, the heat capacity of liquid with eutectic composition was investigated by Schmid and Sommer [34]. Besides that, Brebrick [11] measured a partial pressure of $Te_2$ over alloys with compositions varies from 44 to 70 at% Te. Thermodynamic description of the binary Bi-Te system was proposed by Mao et al. [5]; however, in their proposition the substitional solution model was used for describing liquid phase what seems to be a simplification that doesn't take into consideration existence of a liquid associate. Moreover, Mao et al. [5] omitted modeling of homogeneity range of Bi2Te3 phase what is crucial for thermoelectric material modeling.

## 3. Thermodynamic models

Keeping Mao et al. [5] description of Bi-Te equilibria, following phases are considered in this work: liquid, Rhombohedral_A7 (Bi), Hexagonal_A8 (Te), $Bi_2Te_3$, Beta, $Bi_2Te$, and $Bi_4Te_3$. Detailed information about these phases is given in Table 1.

The Gibbs free energies of pure elements with respect to temperature ${}^0G_i(T) = G_i(T) - H_i^{SER}$ are represented by Eq. 2:

$$ {}^0G_i(T) = a + bT + cTln(T) + dT^2 + eT^{-1} + fT^3 + iT^4 + jT^7 + kT^{-9} \tag{2} $$

The ${}^0G_i(T)$ data are referred to the constant enthalpy value of the standard element reference $H_i^{SER}$ at 298.15 K and 1 bar as recommended by Scientific Group Thermodata Europe (SGTE) [35]. The reference states are: Rhombohedral_A7 (Bi), Hexagonal_A8 (Te). The expression may be given for several temperature ranges, where the coefficients *a, b, c, d, e, f, i, j, k* have different values. The ${}^0G_i(T)$ functions are taken from SGTE Unary (Pure elements) TDB v.5 [35].

**Table 1**
Crystal structures of phases in Bi-Te system.

| Phase | Pearson symbol | Space group | References |
|---|---|---|---|
| Rhombohedral_A7 (Bi) | hR6 | $R\bar{3}m$ | [9] |
| Hexahonal_A8 (Te) | hP3 | $P3_121$ | [9] |
| $Bi_2Te_3$ | hR5 | $R\bar{3}m$ | [42] |
| Beta | – | – | – |
| $Bi_2Te$ | hP9 | $P\bar{3}m1$ | [43] |
| $Bi_4Te_3$ | hR7 | $R\bar{3}m$ | [44] |

**Table 2**
Thermodynamic parameters obtained in this work.

| Phase | Parameter |
|---|---|
| Liquid | ${}^0G_{Bi_2Te_3}^{Liquid} = -72794.5 - 28.082T + 2GLIQBI + 3GLIQTE$ |
| | ${}^0L_{Bi,Bi_2Te_3}^{Liquid} = 15927.8 + 1.593T$ |
| | ${}^0L_{Bi_2Te_3,Te}^{Liquid} = -258620.9 + 134.6T$ |
| | ${}^1L_{Bi_2Te_3,Te}^{Liquid} = -140786 + 153.522T$ |
| $Bi_2Te_3$ | ${}^0G_{Bi:Bi}^{Bi_2Te_3} = 150000 + 5GHSERBI$ |
| | ${}^0G_{Te:Bi}^{Bi_2Te_3} = 0$ |
| | ${}^0G_{Bi:Te}^{Bi_2Te_3} = -95435.54 + 18.70T + 2GHSERBI + 3GHSERTE$ |
| | ${}^0G_{Te:Te}^{Bi_2Te_3} = 150000 + 5GHSERTE$ |
| | ${}^0L_{Bi:Te:*}^{Bi_2Te_3} = 50000 - 201T$ |
| | ${}^0L_{*:Bi,Te}^{Bi_2Te_3} = 45000 - 205T$ |
| Beta | ${}^0G_{Bi:Bi}^{Beta} = 7371.29 + 48.735T + 5GHSERBI$ |
| | ${}^0G_{Bi:Te}^{Beta} = 1162.35 + {}^0G_{Bi:Te}^{Bi_2Te_3}$ |
| | ${}^0L_{Bi:Bi,Te}^{Beta} = -30963.5 - 79.783T$ |
| | ${}^0L_{Bi:Bi,Te}^{Beta} = -4387.95 - 27.642T$ |
| $Bi_2Te$ | ${}^0G_{Bi:Te}^{Bi_2Te} = -32016.98 - 5.762T + 2GHSERBI + GHSERTE$ |
| $Bi_4Te_3$ | ${}^0G_{Bi:Te}^{Bi_4Te_3} = -96295.22 - 6.906T + 4GHSERBI + 3GHSERTE$ |

### 3.1. *Rhombohedral_A7 (Bi), Hexagonal_A8 (Te) terminal phases*

Experimental information doesn't indicate neither solubility of Bi in Te nor Te in Bi. Therefore, both phases were treated as pure elements and their Gibbs energies were taken directly from the unary elements database [35].

### 3.2. *$Bi_2Te$ and $Bi_4Te_3$ phases*

Both phases were treated as line compounds and their Gibbs energies were modeled as follows:

$$ {}^0G_{Bi:Te}^{Bi_mTe_n} = a + bT + m*GHSERBI + n*GHSERTE \tag{3} $$

where *a* and *b* are adjustable parameters, *T* is an absolute temperature, *m, n* are stoichiometric coefficients and *GHSERBI* and *GHSERTE* are Gibbs energies of Bi and Te in their SER reference state, respectively.

### 3.3. *$Bi_2Te_3$ phase*

Gibbs free energy of binary stoichiometric $Bi_2Te_3$ compound is described by Wagner-Schottky defect model [36]. The model describes the variation of the composition range as a function of various defects. In this case the anti-site atoms defect describes very small homogeneity range of $Bi_2Te_3$ intermetallic compound as (Bi,Te)2:(Bi,Te)3, what is in agreement with deliberation given by Xu et al. [12]. Then Gibbs free