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Using thermo-calc software to produce the phase diagram of Zn-Te system

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Abstract: In this work, Thermo-Calc software 2019b is used to recalculate the liquidus-solidus phase diagram of the Zn-Te binary system. The produced phase diagram is in good agreement with the experimental results found in the literature, and it shows five stable phases, which are elemental Zn, elemental Te, ZnTe compound, Zn liquid, and Te liquid. A monotectic reaction is observed at monotectic temperature of 1479.14 K and 59.369 Zn mole percent, and a miscibility gap is found between 59.369 and 97.2781 Zn mole percent above the monotectic temperature. Moreover, there are two eutectic reactions at the Te and Zn terminals. From this phase diagram, the maximum solubility of ZnTe in liquid Zn is determined as 2.7219% at 1479.14 K. The melting points of Te, Zn, and stoichiometic ZnTe are found to be 722.587 ± 0.025 K, 692.680 ± 0.025 K, and 1568.400 ± 0.025 K respectively. These results are important for the development of preparation methods of ZnTe, which is important for several industries including solar cells.

Keywords: *Phase diagram, Solar cells, Thermo-calc software, Zinc tellurid,. Zn-Te binary system*

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1. INTRODUCTION

Knowledge of the phase diagram is essential for improvement of the materials properties, and development of preparation methods. Zn-Te binary system is one of the Zn-chalcogen systems (i.e. Zn-Te, Zn-Se, and Zn-S). These systems are of considerable technological importance due to the semiconducting properties of the compounds ZnTe, ZnSe and ZnS [1], which are of potential use in building electronic devices [2] and solar cells due to their interesting physical, electrical, and optical properties. The Zn-Te system is very important in building electronic and optoelectronic devices. ZnTe is the sole intermediate compound in the Zn-Te binary system, and this compound has a direct band gap of 2.26 eV at room temperature [3], and low electron affinity of 3.53 eV [4]. ZnTe has a cubic zincblende structure with space group $F4\bar{3}m$ and lattice constant a = 6.101 Å [5]. It has a p-type electrical conductivity which makes it a favorable p-type buffer layer in Cd-based hetero-junction solar cells [6,7]. The crystal of ZnTe has a good sensitivity in the green spectral region, which makes this material attractive for use in the fabrication of optoelectronic devices [4,8]. ZnTe is very important for different technologies such as optoelectronic and thermoelectric device technologies, in addition to solar cells and green-light-emitting diodes [9]. It is also used as a back contact [10] to CdTe-based solar cells in the superstrate device structure, and a buffer layer in these CdTe thin film solar cells. This is because of its chemical stability and the near-perfect alignment of its valence band gap and that of CdTe which, enables facile hole transport [11,12]. It is also used as the first unit in a tandem solar cell, a buffer layer for an HgCdTe infrared detector, and as a part of the graded p-Zn(Te)Se multiquantum-well structures in a blue-green laser diode [13-16].

The phase diagram of Zn-Te binary system was produced by several authors such as [1,2,17]. Haloui et al. [17] determined it experimentally, and Feutelais et al. [2] calculated it with the program BINFKT [18]. However, these works are old, where they were published in 1997, and there are discrepancies between the results. The objective of this work is to produce a liquidus-solidus equilibrium phase diagram of ZnTe using the most recent database impeded in the Thermo-Calc software 2019b, and to compare the results with the results found in the literature. The importance of this study is inherent in; first, the importance of this phase diagram as a basis of crystal growth from melting substance, so it can benefit in improving preparation methods, and second in the importance of ZnTe for the industry of optical devices such as the yellow and green light emitting diodes and laser diodes, and the industry of optoelectronic devices such as electro-optical sensors [19] and solar cells.

2. METHODOLOGY

Thermo-Calc is a robust and flexible software and database package for all types of thermodynamic assessments such as phase equilibrium, phase diagram, and phase transformation calculations. In addition, with its application-oriented interface, many types of process simulations can be implemented [20]. Thermo-Calc software-2019b- is used to perform different kinds of thermodynamic and phase diagram calculations in equilibrium problems by the Calphad method [21], where this word was derived from the phrase (CALculation of PHAse Diagrams). The software is based upon a powerful Gibbs Energy Minimizer that utilizes Gibbs free energy minimization procedure to calculate phase equilibria and thermodynamic properties of a chosen system. The Calphad method is based on deriving the thermodynamic functions of a system from all available experimental data, where the thermodynamic functions are represented as polynomials of chemical composition and temperature. Then, the values of the polynomial coefficients are obtained using numerical optimization techniques [22,23]. The Thermo-Calc software has two main components: the application itself, and the internally-consistent thermodynamic dataset it uses. For a given set of conditions, the computer determines the change in free

energy for each possible combination of phases and phase compositions. Then, it selects the state that minimizes the total Gibbs free energy [24].

In this work as in the previous works [25-30], the template "Binary Calculation" with the type of calculation "phase diagram" was chosen to calculate the equilibrium phase diagram of the Zn-Te binary system. The total pressure is 1 bar, and temperature ranges are automatically selected. The used database is the TCBIN: TC Binary Solutions v1.1 database and just stable phases were credited.

3. RESULTS AND DISCUSSION

Fig.1a shows the liquidus-solidus phase diagram obtained in this work using Thermo-Calc 2019b Software. The phase diagram shows five stable phases, and seven fields; one single-phase field and six fields of two mixed phases, in addition to an intermediate compound line. The phases are Te solid (TRIGONAL_A8), Zn solid (HCP_ZN), ZnTe solid (B3_ZINCBLENDE) which is the line compound, Te liquid solution (LIQUID#2) which is the chalcogen-rich solution (Zn in Te) with constituents; Te, ZnTe, and Zn, and Zn liquid solution (LIQUID) which is the metal-rich solution (Te in Zn) with constituents; Zn, ZnTe, and Te. There are dormant gas phases that consist of (Te, ZnTe, Te_2, Te_3, Te_4, Te_5, Te_6, Te_7, and Zn), and they appear after high temperatures and depend on Zn mole percent. These phases don't appear in the phase diagram because they are not stable.

The one phase field is a liquid, and it appears in the upper part of the phase diagram as a white region, where this field extends over the whole composition range. The fields of two mixed phases are; Te solid + ZnTe solid or (B3_ZINCBLENDE+TRIGONAL_A8) between 0-50 Zn mole percent and 300 K to the melting temperature of Te, (Zn solid + ZnTe solid) or (B3_ZINCBLENDE+HCP_ZN) in the region restricted between 50-100 Zn mole percent and temperature range 300 K to melting temperature of Zn, (Te liquid+ ZnTe solid) or (LIQUID#2+B3_ZINCBLENDE) in the region between the melting points of Te and ZnTe and 0-50 Zn mole percent, (Zn liquid + ZnTe solid) or (LIQUID+B3_ZINCBLENDE) in the region limited by 50-100 Zn percent and melting temperatures of Zn and ZnTe, (Te liquid + ZnTe solid) or (LIQUID#2+B3_ZINCBLENDE) limited by 50-59.369 Zn mole percent and temperature range 1205.99-1568.400 K, and finally (liquid Te + liquid Zn) or (LIQUID+LIQUID#2) in the region between 59.369-97.2781 Zn mole percent.

Fig.1b shows the experimental phase diagram of Zn-Te binary system obtained by Haloui et al. [17]. By Comparing Fig.1a with Fig.1b, it is found that there is good agreement between the present work and experimental work of Haloui et al. [17], where both phase diagrams have the same shape, show the same phases, and the same number of fields.

From Fig.1a, the melting points of Te and Zn are 722.587 ± 0.025 K and 692.680 ± 0.025 K respectively, while the temperature of the congruent melting of stoichiometric ZnTe is 1568.400 ± 0.025 K. These melting temperatures of pure elements are very close to the values found in [31], where the melting point of Te is 722.66 K and that of Zn is 692.677 K. The melting point of ZnTe is approximately the same as the one obtained by Glazov and Pavlova [32], which is 1568 K, but it is far from both the experimental value recorded by Feutelais et al. [2] which is T= 1563 ± 8 K, and the calculated value obtained by them, which is 1570 K. The melting temperature of ZnTe obtained in this work is the same as the accepted value, which is 1568 K [33], and this consistency is mainly due to the most recent database implemented in Thermo-Calc 2019b.

In addition, Fig.1a shows that there is a monotectic reaction:

$$Liquid\ \#2 \xrightarrow{Cooling} Liquid\ +\ ZnTe\ (B3\_ZINCBLENDE) \qquad (1)$$

where the monotectic temperature is 1479.14 K at 59.369 Zn mole percent. This reaction was experimentally determined by Feutelais et al. [2] at T = 1480 K. After this point (as seen in Fig.1a), there is a miscibility gap on the Zn rich side between 59.369 and 97.2781 Zn mole percent above T = 1479.14 K, where the liquid solutions: liquid Te (Liquid #2) and liquid Zn (liquid) are present in equilibrium, and they are immiscible in each other. The miscibility increases with temperature, and after 1855.75 K both liquids are completely miscible in each other and a homogeneous liquid is formed.

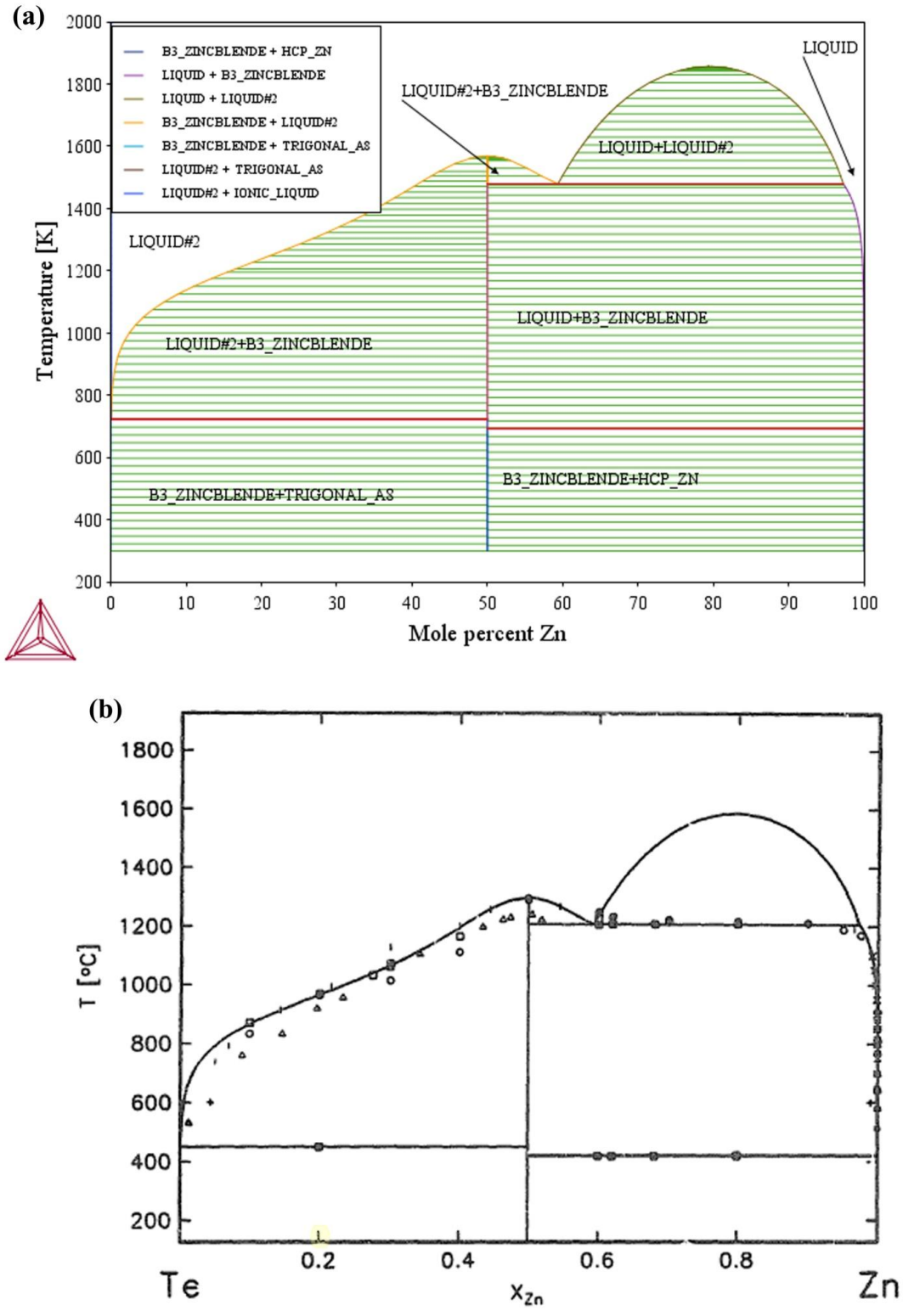

Figure 1. The phase diagram of Zn-Te binary system. a) Computed in this work using Thermo-Calc -2019b. b) Obtained experimentally. Reprinted after Haloui et al. [17]. Copyright © 1997 Published by Elsevier B.V.

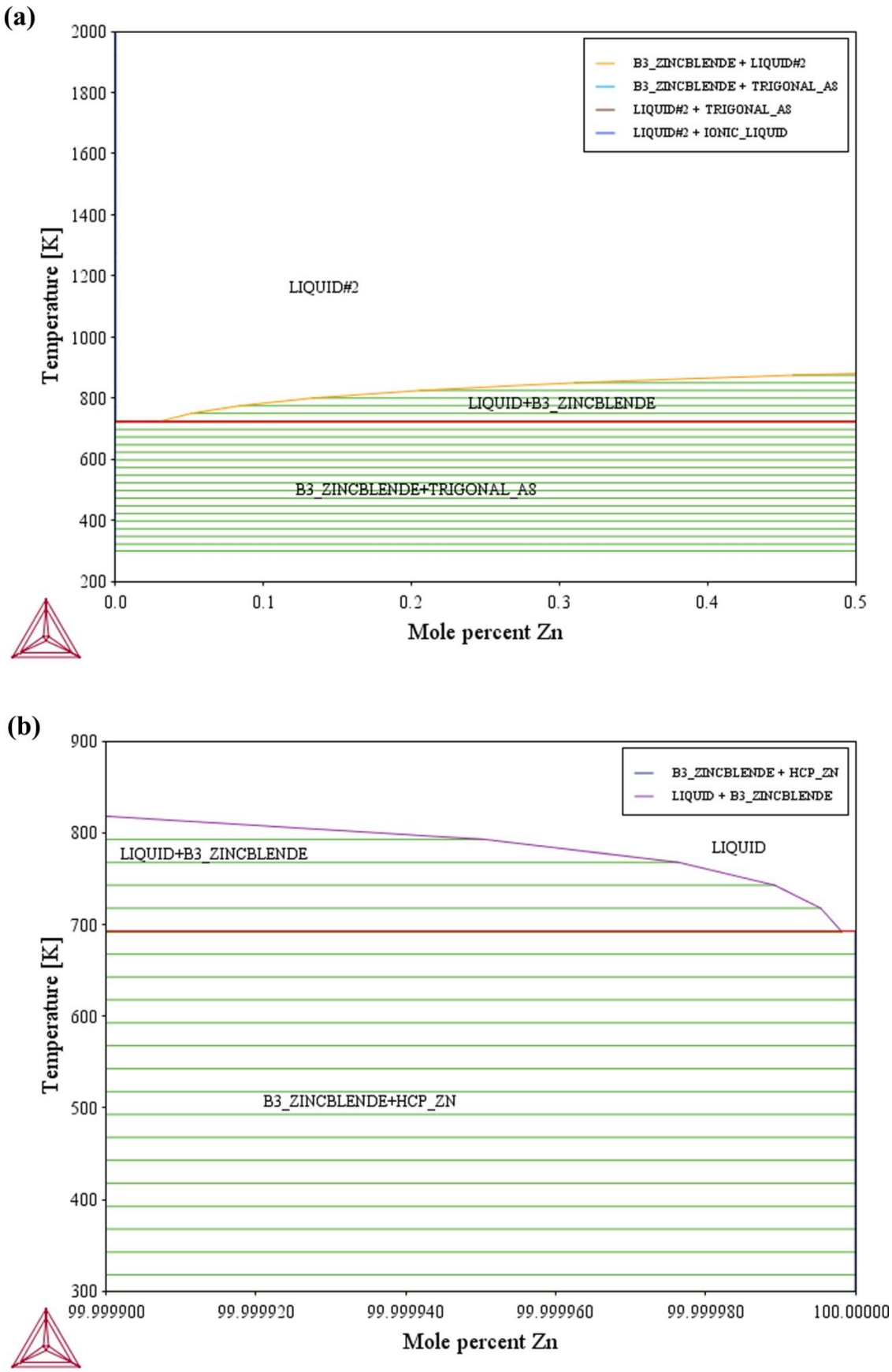

Figure 2. Enlarged portions of the phase diagram in Fig.1a to show eutectic reactions. a) Te- rich side. b) Zn-rich side.

Fig.2 displays enlarged portions of the terminals in Fig.1a, where Fig.2a shows the Te rich terminal and Fig.2b shows the Zn-rich terminal. There are two degenerate eutectic reactions; the first one as seen in Fig.2a is:

$$Liquid\ 2 \rightleftarrows Te + ZnTe \qquad (2)$$

which takes place at T=722.587 ± 0.025 K, and 0.029 Zn mole percent. This result is approximately the same as the result of Feutelais et al. [2] who recorded this reaction experimentally at T= 449.0 ± 0.5 °C which corresponds to 722.15 K, and by computation at 449.4 °C (722.55 K).

The second reaction as seen in Fig.2b is:

$$Liquid \rightleftarrows Zn + ZnTe \qquad (3)$$

at 692.680 ± 0.025 K and about 100 Zn mole percent. This result is slightly higher than the experimental result obtained by Feutelais et al. [2] who recorded this reaction experimentally at T= 418.7 ± 0.5 °C which corresponds to 691.85 K, but very close to their result obtained by computation at 419.6 °C (692.75 K).

The mutual solid solubilities of Zn and Te is essentially zero [23]. From Fig.2b the solubility of ZnTe in liquid Te starts from the melting point of Te and continues until 1855.75 K, and the solubility of ZnTe in liquid Zn starts at the melting temperature of Zn. The maximum solubility of ZnTe in liquid Zn obtained from Fig.2b is 2.7219% at 1479.14 K, andt There are no experimental or computational numbers in the literature to compare this result with them.

4. CONCLUSION

The phase diagram of the Zn-Te binary system was recalculated using Thermo-Calc 2019b software. The phase diagram showed five stable phases, which are; elemental Zn and Te, ZnTe compound, liquid Zn and liquid Te. Melting points of Zn, Te, and ZnTe are determined and compared with experimental values found in the literature. Two degenerate eutectic reactions at the Zn and Te terminals and a monotectic reaction is found at 1479.14 K and 59.369 Zn mole percent. A miscibility gap is observed in the range 59.369-97.2781 Zn mole percent above the monotectic temperature, where the two liquids (liquid Zn and liquid Te) are immiscible in each other. The maximum solubility of ZnTe in liquid Zn is determined as 2.7219% at 1479.14 K.

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