Thermodynamics of the S-Sn system: Implication for synthesis of earth abundant photovoltaic absorber materials

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Note: *Supporting Information* (SI) included.

ABSTRACT: Development of earth-abundant, non-toxic, and environmentally friendly thin-film photovoltaic (PV) absorber materials motivates the present thermodynamic study of the S-Sn system, which is modeled using the CALPHAD (CALculation of PHase Diagram) technique aided by first-principles calculations. The temperature-composition (T - x), pressure-composition (P - x) and pressure-temperature (P - T) phase diagrams obtained from the modeling identifies stability regions for different tin sulfides. This provides quantitative information regarding growth windows and annealing conditions for intelligent discovery and design of synthesis routes to produce low-cost, high-efficiency thin film PV absorber materials such as SnS, SnS₂, Sn₂S₃, and Cu₂ZnSn(S,Se)₄.

Keywords: SnS; CZTS; phase diagrams; first-principles calculations

1. INTRODUCTION

Increasing demand for sustainable energy has motivated research aimed to develop thin-film photovoltaic (PV) absorber materials containing earth abundant, non-toxic, and cost-effective raw materials (Kodigala, 2014). PV absorber materials that show promise include tin (Sn) chalcogenides such as the kesterites $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) or $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) and tin sulfides such as the orthorhombic SnS, all of which possess suitable band gap energy with high absorption coefficient (Buchenau et al., 1971; Kodigala, 2014; Noguchi et al., 1994; Ogah et al., 2009; Sajeesh et al., 2010). Currently, the highest energy conversion efficiencies are 12.6 % for CZTSSe (Wang et al., 2014) and 4.4 % for SnS (Sinsermsuksakul et al., 2014; Steinmann et al., 2014), which are considerably lower than the theoretical Shockley-Queisser limit (Kodigala, 2014; Shockley and Queisser, 1961). It is expected that an efficiency of at least 15 % is required for these earth abundant PV materials to be competitive with commercial $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$ and CdTe solar cells with champion efficiencies of 20.5 % and 19.6 %, respectively (Green et al., 2014). Consequently, researchers within the field are facing a great challenge to develop new and more advanced technical solutions regarding the syntheses of SnS and CZTS-based PV devices.

Examination of different routes used for production of CZTS-based devices indicates that the solar cells showing high efficiency have been fabricated by pathways that include reaction of metal or metal sulfide precursor in a sulfur (S) atmosphere (Ahmed et al., 2012; Katagiri et al., 2008; Shin et al., 2013) or by double-stage physical vapor deposition (Romero et al., 2011; Schubert et al., 2011), both of which involve an annealing treatment at elevated temperature, typically around 823 K. The annealing seems to be necessary to homogenize the structure. Prevention of CZTS decomposition at this high temperature is critical for successful absorber

synthesis (Redinger et al., 2011a, 2011b; Scragg et al., 2011). This requires specification of the process variables including the temperature, sulfur and SnS partial pressures, total chamber pressure as well as the overall metal composition. Defining these conditions empirically in this four-component system is challenging and hence, an understanding of equilibrium phase relations to predict the stability window for CZTS would assist greatly the search for optimal processing conditions.

A detailed knowledge of the phase relations also in the S-Sn phase diagram would be useful to provide guidance on the preparation of CZTS thin films. Under conditions for which the CZTS phase is not stable, it decomposes into its binary sulfides (Scragg et al., 2011) Cu_2S , ZnS , and SnS . Of these, SnS has the highest vapor pressure. Experimental observations suggest that SnS first forms as a solid phase on the CZTS film surface and then sublimates during the annealing step (Scragg et al., 2011). Ideally, the decomposition should be prevented or reversed by maintaining an ambient gas at higher tin and sulfur chemical potentials than their equilibrium values (Redinger et al., 2011a, 2011b).

Furthermore, the binary compound SnS has attracted interest in its own right as a relatively unexplored earth-abundant and non-toxic PV material (Biacchi et al., 2013). Important to PV applications, this compound shows p-type behavior, reportedly due to tin vacancies, and high absorption coefficient above the direct absorption edge at 1.3-1.5 eV (Buchenau et al., 1971; Noguchi et al., 1994; Ogah et al., 2009; Sajeesh et al., 2010). Furthermore, given its simpler chemistry than the multicomponent CZTS, the processing should be more straightforward.

SnS crystallizes in an orthorhombic unit cell composed of double SnS layers perpendicular to the b axis with tin and sulfur atoms covalently bonded within the layers and the layers bonded by the weak van der Waals bonds (Albers et al., 1961). These double layers are expected to give rise to a chemically inert surface with few surface states (Avellaneda et al., 2007) making it defect-tolerant. It is suggested that this might reduce the carrier recombination loss due to defects at p-n junctions or at grain boundaries, and hence, prolong the carrier lifetime (Sinsermsuksakul et al., 2011). Although limited experimental effort has been devoted to SnS PV device fabrication, ~4.4 % devices have been demonstrated (Sinsermsuksakul et al., 2014). Various techniques for depositing SnS have been reported including thermal evaporation (Hartman et al., 2011; Johnson et al., 1999; Koteeswara Reddy et al., 2007; Miles et al., 2009; Nebesny et al., 1991; Steinmann et al., 2014; Wang et al., 2012), spray pyrolysis (Calixto-Rodriguez et al., 2009; Khadraoui et al., 2010; Sajeesh et al., 2010), [sputtering from SnS and SnS₂ targets \(Banai et al., 2015, 2013\)](#) and metalorganic chemical vapor deposition (Bade et al., 2008; Barone et al., 2002, 2001; Hibbert et al., 2001; Price et al., 1999; Sinsermsuksakul et al., 2014). In each of these processes, understanding the thermodynamics of the S-Sn system is important to identify appropriate growth regions and annealing conditions to avoid formation of other binary compounds (i.e., SnS₂ and Sn₂S₃) (Banai et al., 2015; Barone et al., 2001; Mathews et al., 2010; Miles et al., 2009; Price et al., 1999; Sinsermsuksakul et al., 2014), and to increase the understanding of the point defect chemistry and hence defining process conditions that lead to suitable electrical properties.

It is noted that Sn₂S₃ and SnS₂ are also useful materials. Sn₂S₃ exhibits a band gap of 0.95 eV (Sánchez-Juárez et al., 2005) and has been suggested as suitable for nearly lattice-matched heterojunctions with CdTe, GaSb, and AlSb, which find applications in the detection and

generation of infrared radiation (Khadraoui et al., 2010). Tin disulfide, SnS_2 , with its mid-band gap of 2.18 eV (Schlaf et al., 1997), is of interest for several applications such as window layer material in thin film solar cells (e.g. replacing toxic CdS) (Shi et al., 2013). This again motivates investigation of phase equilibria in the S-Sn system.

The present work aims to develop a full thermodynamic description of the S-Sn system using the CALPHAD (CALculation of PHase Diagram) technique that assesses available experimental data, supplemented by first-principles calculations, to produce a thermodynamically consistent description of phase equilibria (Liu, 2009). The idea with the CALPHAD technique is to assess parameters for functions describing the Gibbs energy of each phase relevant for the system. Once the thermodynamic description has been established, the equilibrium is obtained by minimizing the total Gibbs energy of the system accounting for all phases' contribution at the condition of question. The strength of this approach is the possibility to combine constituent subsystems (unary, binary, ternary etc.) to extrapolate into the multicomponent space. The description can then be used to interpolate and extrapolate among the process variables temperature (T), composition (x), and pressure (P) parameters to rapidly explore operating conditions. The CALPHAD technique has been used extensively and successfully for many types of material systems. For example, it has been an important tool for alloy development of tool steels (Frisk et al., 2005; Lindwall and Frisk, 2013), Ni-base superalloys (Campbell et al., 2002; Kattner, 2002; Saunders et al., 2000) as well as to model complex behavior of oxides (Kjellqvist and Selleby, 2010; Kjellqvist et al., 2008; Lindwall et al., 2015) and cemented carbides (Ekroth et al., 2000; Frisk et al., 2005). Another example relevant for the current work, is the boron-magnesium (B-Mg) system (Liu et al., 2001b) where the developed description was used to calculate T - x , P - x

and P - T diagrams for the purpose to guidance when selecting process condition for preparation of MgB_2 superconductor films (Liu et al., 2001a).

Although some experimental information as well as some theoretical investigations are available for the thermodynamics of the S-Sn system, no CALPHAD description has hitherto been developed and hence, the information yet available is limited to the particular conditions of investigation. Based on CALPHAD modeling of the S-Sn system performed in the present work, the assessed T - x , P - x , and P - T phase diagrams are generated and their applications are discussed.

2. THERMODYNAMICS OF THE S-SN SYSTEM

The type of phases, their amount and composition, that lead to the minimal Gibbs energy of the total system represents the equilibrium state of the system at given conditions and is obtained, in the case of the CALPHAD method, by minimization taking the energy contribution from all modeled phases into account. Experimentally, it is known that the S-Sn system contains four solid solution phases (α -S, β -S, α -Sn and β -Sn), a liquid phase with two miscibility gaps, a gas phase and a number of Sn sulfides (SnS , Sn_2S_3 and SnS_2) with several allomorphs and very narrow homogeneity ranges. Hence, these are the phases that are modeled in the present work. Due to limited data, only one stoichiometric sulfide at each sulfur composition for both Sn_2S_3 and SnS_2 , and the two equimolar allomorphs, α - and β -SnS are modeled. For the liquid phase, the associated model (Lukas et al., 2007) is adopted with the fictive species SnS. The details are presented in the Supporting Information, including (i) the review of phase equilibria and thermochemical data in the literature; (ii) thermodynamic modeling of S-Sn system using the Thermo-Calc software (Andersson et al., 2002); (iii) first-principles calculations of equilibrium properties for elements and compounds in the S-Sn system using the Vienna Ab-initio

Simulation Package (VASP) code (Kresse and Furthmüller, 1996); and (iv) the modeling parameters and first-principles results.

Figure 1 compares the calculated temperature-composition (T - x) phase diagram at 1 bar pressure with the reported experimental data (Albers and Schol, 1961; Anderson and Ridge, 1943; Biltz and Mecklenburg, 1909; Moh, 1969). The calculated diagram is a result of a Gibbs energy minimization where the elemental phases (α -S, β -S, α -Sn and β -Sn), the liquid, and the intermediate compounds SnS (α -SnS and β -SnS), Sn_2S_3 and SnS_2 are included; i.e. the gas phase has not been incorporated. The experimental invariant transition temperatures and compositions are listed in Table 1 in comparison to the values calculated using the developed CALPHAD description. This table shows that the assessed T - x phase diagram reproduces the experimental observations within the experimental uncertainty with one exception. The invariant reaction associated with liquid (L) and SnS_2 , on the S-rich side of the diagram (i.e. $\text{L}_2 \leftrightarrow \text{L}_3 + \text{SnS}_2$ in Figure 1) shows a slightly higher calculated temperature (1133 K) than the measured value (1114 K) (Moh, 1969).

A transition with a difference between the experimental and assessed values but within the experimental uncertainty is the measured temperature for the eutectic reaction $\text{L}_2 \leftrightarrow \text{SnS} + \text{Sn}_2\text{S}_3$ at ~55 at.% sulfur (Albers and Schol, 1961; Karakhanova et al., 1966; Moh, 1969), with the three measured values higher than the calculated one (967 K). The latter deviation is accepted in the optimization on the basis of the large scatter in the experimental measurements; see details in Table 1. In the case of the discrepancy for the invariant reaction associated with the liquid (L) and SnS_2 on the S-rich side, it is argued that only one set of data is available and that the high volatility of sulfur can lead to significant experimental error.

Figure 2 illustrates the predicted T - x phase diagrams at three different pressures (1 bar, 1 mbar, and 0.001 mbar). In the calculations for these diagrams, a description of the Gibbs energy of the gas phase is also incorporated in the minimization to find the equilibrium, in addition to the phases included in Figure 1. The gas phase is treated as ideal, see Supporting Information, and the species S, S₂, S₃, S₄, S₅, S₆, S₇, S₈, Sn, and Sn₂, SnS, SnS₂, and Sn₂S₂ are included, using the Gibbs Energy recommendations provided in the SGTE Database (“SGTE Substances Database version 4,” 2008). For the pressure of 1 bar (Figure 2a), the gas phase is stable above ~735 K on the S-rich side, which is a temperature similar to the experimentally measured boiling temperature for pure sulfur (717.8 K) (Meyer, 1976). As the pressure decreases, the stability region for gas increases and the sublimation temperature for the compounds decreases (Figures 2b and 2c). Note that the order of the sublimation temperatures for the SnS₂ and the Sn₃S₂ compounds changes as the pressure is decreased. SnS₂ is stable up to a higher temperature compared to the Sn₂S₃ at higher pressure, whereas Sn₂S₃, due to its lower sulfur content, is the thermally more stable sulfide at lower pressure.

3. APPLICATIONS AND DISCUSSION

As discussed in the Introduction, a motivation for developing a thermodynamic model describing phase equilibria in the S-Sn system is to provide guidance when growing and annealing tin sulfide films. Furthermore, synthesis of CZTS materials often involves a high temperature annealing step while avoiding decomposition of the CZTS phase. Thus mapping the stability ranges as a function of temperature, pressure and ambient gas phase composition that, at least, stabilizes the CZTS decomposition product SnS is needed. A typical annealing temperature for

CZTS films is about 823 K, and in Figure 3, a P - x diagram for the S-Sn system is provided at this temperature. This P - x phase diagram is calculated using the thermodynamic description of the S-Sn system presented in the Supporting Information, and the diagram indicates the stable phases as pressure and composition combinations are varied at 823 K. The phase relations and phase compositions depend strongly on the S/Sn ratio in the system. For sulfur contents below 50 at.%, the liquid phase is stable over the whole investigated pressure range; at lower pressures it is stable together with the gas phase and at higher pressures it is stable together with the α -SnS. If the composition is on the S-rich side, the three sulfide compounds are in equilibrium with the gas phase except for the two two-phase regions " α -SnS + SnS₂" and "SnS₂ + Sn₂S₃" at higher pressure.

The minimum pressure required to stabilize the tin monosulfide, α -SnS, is 2.4×10^{-3} mbar according to the calculation and occurs at the S/Sn ratio of 1:1. This can be compared with the experimental vapor pressure of pure SnS at 823 K which is 2.5×10^{-3} mbar in accordance to the measurements by (Piacente et al., 1991). With increasing S content; i.e. as the S/Sn ratio changes towards the S-rich side, the minimum total pressure required to stabilize the SnS increases. This is due to larger partial pressure of tin that is required to meet the increased partial pressure of sulfur that the increased sulfur content leads to. Consequently, the total pressure increases. As the chemical activity of sulfur is high enough, the S-richer compound Sn₂S₃ becomes stable which, at 823 K, occurs at the total pressure of 1.4×10^{-2} mbar. At an even higher sulfur activity, the SnS₂ compound can become stable. This occurs at the total pressure of 0.776 mbar. In this way the stability regions "gas (G) + α -SnS", "G + Sn₂S₃" and "G + SnS₂" at 823 K are identified in the P - x diagram as shown in Figure 3.

In the work by (Banai et al., 2015), the present CALPHAD description is utilized to calculate P - x phase diagrams such as the ones in Figure 3, but at 573, 473 and 373 K. (Banai et al., 2015) prepared α -SnS thin films by sputtering from a SnS₂ target followed by annealing in an atmosphere close to vacuum ($\leq 10^{-6}$ mbar) to transform the S-rich film into α -SnS by sulfur evaporation. As expected, the resulting thin film microstructure was strongly correlated to the annealing conditions and the different outcomes could be understood by studying calculated P - x phase diagrams. It was concluded that a temperature of approximately 673 K was most appropriate for the current experimental setup ($\leq 10^{-6}$ mbar).

The above discussion concerns the pressure required for stabilizing Sn sulfides; i.e. not the CZTS phase. For CZTS, (Scrugg et al., 2011) combined experimental investigations with a kinetic model to determine the gas ambient conditions that establish dynamic equilibrium at the CZTS surface. Their results suggest that the product $P^c(\text{SnS}) \cdot P^c(\text{S}_2)^{1/2}$, where $P^c(\text{SnS})$ and $P^c(\text{S}_2)$ are the partial pressures of SnS and S₂ in gas, should be $(3.8 \pm 1.2) \cdot 10^{-5} \text{ mbar}^{3/2}$ or greater at 823 K to ensure stability of the CZTS phase. Here, $P^c(\text{SnS})$ and $P^c(\text{S}_2)$ are the partial pressures of SnS and S₂ in the gas above CZTS. In their model, they assumed that SnS first forms as a solid phase on the CZTS surface and further, assumed that the value of $P^c(\text{SnS})$ thus could be taken to be the same as the equilibrium pressure over a pure SnS sulfide surface, $P(\text{SnS})$, which had been previously measured (Piacente et al., 1991). By experimentally determine the extent of the CZTS decomposition at known SnS and S₂ partial pressures, they could then estimate a critical value for the additional S₂ pressure, $P^c(\text{S}_2)$, required for stabilizing CZTS. The S-Sn description developed here could be used to further refine such an empirical model as undesired approximations due to limited thermodynamic data available in the literature could be avoided.

For example, the value for $P(\text{SnS})$ can be obtained at any temperature of importance using the present description. For ultimate control of CZTS process parameters, however, a complete thermodynamic description of the CZTS/CZTSSe system would be required and the binary S-Sn subsystem developed here is only one of the necessary step stones for the development of this multicomponent description.

Deposition of a single-phase film, SnS, SnS₂ or Sn₂S₃, becomes favorable when the growth conditions (substrate temperature together with sulfur and tin overpressures) fall within the window where the thermodynamically stable phases are the desired sulfide and the gas phase. Within this growth window, the sulfide does not decompose and the excess tin and sulfur do not condense on the film surface and thus, the formation of the film is adsorption-controlled. The single-phase growth window can be inferred from T - x and P - x phase diagrams like the ones shown in Figures 2 and 3, but is more clearly illustrated in a P - T diagram. In this case, the overall S/Sn ratio is kept constant, similar to our early work on the adsorption-controlled growth window of the MgB₂ superconductor film (Liu et al., 2001a, 2001b). Three such diagrams are shown in Figure 4 for different compositions on the S-rich side; i.e. at 55, 75, and 95 at.% sulfur. For S/Sn combinations on the Sn-rich side, the liquid phase is stable for most conditions above the melting point of tin. This is true also at lower pressures which, for example, can be seen in Figure 2c, where the T - x phase diagrams at 10⁻³ mbar, is shown. The boiling temperature of tin is high (around 2860 K at 1 bar and around 1340 K at 10⁻³ mbar) and to have solid α -SnS stable together with only gas at conditions regarded as achievable experimentally cannot be expected. S/Sn ratios should therefore be avoided in preparation routes where the presence of liquid would be detrimental. The presence of a liquid phase, if completely wetting, would present a mass transfer barrier during film growth to limit growth rate and likely leave the surface rough upon

cooling to room temperature due to depletion of sulfur from the liquid phase as SnS forms and eventual solidification of a second phase of nearly pure tin close to its melting temperature. If the liquid partially wets the growth surface, the possibility of growing nanostructure by a vapor-liquid-solid mechanism exists. This is the case for adsorption-controlled growth of single-phase films by e.g. thermal evaporation and thus, only diagrams for S-rich system are discussed here.

From a thermodynamic perspective, the window beneficial for growing and stabilizing single SnS₂ films is relatively large. For S/Sn ratios equal to or above the stoichiometric SnS₂ composition, the lower boundary of the stability window for SnS₂ and gas; i.e. the boundary between the phase region marked “gas + Sn₂S₃” and “gas + SnS₂” in Figure 4b and 4c, and is approximately given by,

$$\log(P) = -9\,413/T + 8.321 \quad (1)$$

where P is in bar and T is in Kelvin. As long as the growth condition or annealing conditions lie above this boundary, a single phase SnS₂ is thermodynamically stable. If the $\log(P)$ - $1/T$ combination resides below this line, Sn₂S₃ or SnS phases may form. The logarithm of pressure can be approximated as a linear function of $1/T$ due to the ideal behavior of the gas phase for which an Arrhenius relationship is to be expected.

The growth conditions beneficial for growth of SnS films are much more restricted. The S/Sn ratio should be equal or just above the stoichiometric SnS composition for the stability window to be wide, see the regions “gas + α -SnS” and “gas + β -SnS” in Figure 4a. The further away from the SnS composition, the narrower the stability window becomes (e.g. compare the extent of the “gas + α -SnS” and “gas + α -SnS” regions in Figure 4a and 4b, and the risk for formation

of SnS_2 or Sn_2S_3 increases. The upper growth window boundary for SnS from gas is approximately given by,

$$\log(P) = -10\,859/T + 8.340 \quad (2)$$

which is valid for a pressure and temperature below $1.27 \cdot 10^{-3}$ bar and 967 K for β -SnS and $8.5 \cdot 10^{-5}$ bar and 875 K for α -SnS, respectively, see Figure 4a. The lower growth window boundary for SnS is approximately given by,

$$\log(P) = -A/T + B = -11\,041/T + 7.808 \quad (3)$$

This boundary represents solid SnS in equilibrium with gas and the values of the relationship can be compared to previous reported A and B values based on experimental measurements of the vapor pressure of SnS over solid SnS; e.g. the values $A=10\,794$ and $B=7.456$ (from 875 to 1153 K) reported by (Sharma and Chang, 1986) which are comparable to the calculated present values. For more S-rich compositions, the formation of SnS is not thermodynamically possible at all, see Figure 4c. Of course this analysis considers only the equilibrium conditions, and the reaction or mass transfer limitation during growth of the thin film would change the details of the phase stability windows.

4. SUMMARY

A full thermodynamic description of the S-Sn system has been developed using the CALPHAD approach provided with input from the phase equilibrium data in the literature and first-principles calculations reported in this work. Using this description, thermodynamic stability regions of Sn sulfides (SnS , SnS_2 , and Sn_2S_3) are identified and illustrated by temperature-composition (T - x), pressure-composition (P - x) and pressure-temperature (P - T) phase diagrams calculated. These diagrams guide the selection of appropriate conditions for adsorption-

controlled growth of and annealing conditions for single-phase SnS, SnS₂, and Sn₂S₃ films as well as post-deposition annealing conditions for annealing of CZTS-based films while avoiding loss of SnS.

ASSOCIATED CONTENT

Supporting Information

Details of experimental information of the S-Sn binary system available in the literature, first-principles calculations together with structural information, thermodynamic modeling and predicted properties are presented in the Supporting Information. This material is accessible online and free of charge at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by the National Science Foundation (NSF) with Grant Nos. CHE-1230924 and CHE-1230929 and the Gladys Snyder Grant from the College of Earth and Mineral Sciences at the Pennsylvania State University. First-principles calculations were carried out partially on the LION clusters by the Materials Simulation Center and the Research Computing and Cyberinfrastructure Group at the Pennsylvania State University, partially on the resources of NERSC supported by the Office of Science of the U.S. Department of Energy under contract No. DE-AC02-05CH11231, and partially on the resources of XSEDE supported by NSF with Grant No. ACI-1053575.

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FIGURES

(a)

(b)

Figure 1: Calculated temperature-composition phase diagram for the S-Sn system compared to experimental data; ○ (Moh, 1969), + (Anderson and Ridge, 1943), Δ (Biltz and Mecklenburg, 1909) and × (Albers and Schol, 1961). The phase diagram is calculated at the pressure 1 bar and without inclusion of the gas phase. The figure to the right (b) is an enlargement of the central part of the phase diagram to the left (a), and the letter L indicates liquid. Red solid lines represent invariant transformation temperatures.

Figure 2: Calculated temperature-composition phase diagrams for the S-Sn system, including the gas phase, at constant pressures of (a) 1 bar, (b) 1 mbar, and (c) 10^{-3} mbar, with L denoting liquid.

Figure 3: Calculated pressure-composition phase diagram at a typical annealing emperature of 823 K used in CZTS/CZTSSe film growth (Scragg et al., 2011), with L denoting liquid.

(a)

(b)

(c)

Figure 4: Calculated pressure-temperature phase diagrams for the sulfur concentrations of (a) 55 at.%, (b) 75 at.%, and (c) 95 at.%, with L denoting liquid.

TABLES

Table 1: Calculated temperatures (T , in K) and compositions (x_S , in at-%) for invariant reactions and melting (T_m) compared to experimental temperatures and compositions for the S-Sn system.

<i>Reactions</i>	<i>x_S</i>			<i>T</i>
$L_1 \square \beta\text{Sn} + \alpha\text{-SnS}$	-	0	50	505
	-	-	50 ⁱ	504 ⁱ
$L_2 \square L_1 + \beta\text{-SnS}$	46.5	7.1	50.0	1137
	48.0 ^{12, 22}	7.5 ²²	50 ^{j,k,r}	1128, ^r 1131 ^k , 1133 ^{j,p}
$L_2 \square \beta\text{-SnS} + \text{Sn}_2\text{S}_3$	55.7	50.0	60.0	967
	55, ^{k,p} 55.6 ^j	50 ^{j,l,q}	57, ^k 60 ^{j,p}	978, ^l 1013, ^j 1011 ^q
$L_2 + \text{SnS}_2 \square \text{Sn}_2\text{S}_3$	59.1	66.67	60.0	1031
	56.5, ^j 59 ^k	66.67 ^{j,k}	60 ^{j,k}	1018, ^j 1033 ^l
$L_2 \square \text{SnS}_2 + L_3$	69.8	66.67	98.2	1132
	70 ^j	66.67 ^j	98 ^j	1114 ^j
$L_3 \square \text{SnS}_2 + \beta\text{S}$	100	66.67	100	388
	≤ 100 ^j	66.67 ^j	< 100 ^j	385 ^j
T_m for $\beta\text{-SnS}$	50.0			1150
				1143, ⁿ 1148, ^k 1153, ^{j,l,m} 1155 ^o
T_m for Sn_2S_3	60.0			1031
				1018, ^k 1033 ^j
T_m for SnS_2	66.67			1138
				1138, ^j 1143 ^p

ⁱ (Sharma and Chang, 1986)

^j (Moh, 1969)

^k (Karakhanova et al., 1966)

^l (Orr and Christensen, 1958)

^m (Pelabon and Moissan, 1906)

ⁿ (Biltz, 1908)

^o (Biltz and Mecklenburg, 1909)

^p (Albers and Schol, 1961)

^q (Wiedemeier and Csillag, 1979)

^r (Anderson and Ridge, 1943)