Thermodynamic modeling of the PbX (X=S,Te) phase diagram using a five sub-lattice and two sub-lattice model

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ABSTRACT

Five-sublattice and two-sublattice models have been built to describe the PbX (X=S,Te) semiconductors using the CALPHAD method. The five-sublattice model has three additional sublattices to explicitly model interstitials, electrons, and holes. The experimental literature has been critically reviewed and many high temperature carrier concentration results used in previous assessments have been shown to be unreliable. First-principle calculations for the formation energies of neutral defects and their respective ionization energies have also been incorporated into the models. The models show an improvement over previous assessments of PbTe and are the first time PbS has not been treated as a stoichiometric compound in a CALPHAD assessment.

Keywords: CALPHAD, Semiconductors, DFT, Thermoelectric, Pb-Te, Pb-S

1. Introduction

Due to the high demand for energy in today's world, alternative energy resources need to be developed in order to sustain our needs. Thermoelectric (TE) devices provide a viable option, due to their ability to convert waste heat into usable electricity [1]. The measurement of their efficiency is given as a dimensionless figure of merit, ZT, where $ZT = S^2\sigma T/\kappa$ and S , σ , T , and κ are the Seebeck coefficient, electrical conductivity,

temperature, and thermal conductivity, respectively. PbTe has been identified as a high ZT material [2] as well as PbS [3]. The Pb(S,Te) system has also been recognized to further increase the ZT due to introduction of precipitates that help scatter heat-carrying phonons [4]. It is clear that this alloy system could lead to new high ZT materials.

Each of the previously mentioned alloys requires optimization of composition and processing parameters for them to be of use. The parameters used to calculate ZT are often intrinsically linked and separate manipulation of each variable is difficult. However, much work has gone into nanostructuring as a method for reducing the thermal conductivity without lowering the electrical conductivity or the Seebeck coefficient. Nucleation and growth as well as spinodal decomposition as a method for nanostructuring was recently investigated in the Pb(S,Te) system [4]. The experimenters were able to vary the concentration of S in order to induce nucleation or spinodal decomposition. Their study determined that nucleation of a second phase was a much more effective method for scattering heat carrying phonons, thereby reducing the thermal conductivity without adversely affecting the electrical conductivity. The barrier between spinodal decomposition and nucleation and growth at a given temperature is determined where

$\partial^2 G / \partial x^2 = 0$, which can be calculated if the Gibbs free energy of the material is known. To

achieve this, free energies of the two constituent semiconductors is necessary. The CALPHAD method is a well-established technique for building such databases and is a particularly powerful tool for multicomponent systems [5]. It is also a fundamental step in the Integrated Computational Materials Engineering (ICME) process for the optimization of the properties in novel materials [6]. The CALPHAD method is a semi-empirical method that models Gibbs free energy curves to experimental and theoretical information. Recently, the field has seen great success in supplementing experimental information with those obtained through first-principle calculations [7] thereby giving greater physical significance to the models.

The Pb-Te and Pb-S systems have recently been assessed by Bajaj et al. [8] and Huang et al. [9], respectively, however the aim of this paper is to improve the accuracy of the PbX (X=S,Te) semiconductor through a five-sublattice model specifically developed for binary semiconductors [10]. This model can reproduce both phase stability as well as carrier concentrations, which are of the utmost importance for describing electronic materials. This model utilizes both experimental and first-principle calculations and shows a large improvement over previous models. In addition to the 5SL model, a two-sublattice model is also developed for compatibility in multicomponent databases.

2. Literature survey

2.1 Pb-Te

The thermodynamics and off-stoichiometric nature of PbTe has been studied extensively. Due to the extremely narrow homogeneity range of this compound, typical metallographic techniques for measuring the solubility cannot be used. Instead, measurements of the carrier concentration through Hall coefficients, coupled with assumptions of the defects, determine the solubility limits. There are a number of such studies done in this way for PbTe. One of the first such studies was conducted by Brebrick and Allgaier [11]. In this study, ingots of PbTe with either Pb or Te rich compositions were heat treated at various temperatures and quenched. Hall constants were then calculated at room temperature to determine the carrier concentration. A later study by Brebrick and Gubner questioned the previous study's results due to Cu impurities in the Pb-rich samples. The study was repeated; again with Pb-rich and Te-rich ingots and Hall coefficients measured 273 K [12]. In the same year, Scanlon also measured the carrier concentrations at lower annealing temperatures, from 453 K to 673 K [13].

Harman studied the $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$, $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$, and $\text{PbS}_{1-x}\text{Se}_x$ systems through single crystals grown via Bridgman technique [14]. At the same time, Hewes et al. were also investigating the $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ system [15]. Their results largely agreed with previous ones, however, there were large deviations in carrier concentrations at higher temperature in Te-rich samples. The discrepancy was thought to be due to measuring the Hall coefficient at 77 K instead of 273 K. [15]. Despite discrepancies in absolute magnitude, all studies agreed that Te-rich samples exhibited p-type conduction and Pb-rich samples n-type.

An explanation for the discrepancy at high temperature for Te-rich samples was first proposed by Albers et al. [16], who believed that quenching of these materials above a certain temperature was ineffective in maintaining their equilibrium states due to the material's low thermal conductivity. This was finally proved by Mühlberg and Hesse using TEM by confirming the presence of Te precipitates when quenching from high temperature [17]. They determined that the temperature at which equilibrium was not maintained due to inefficient quenching to be approximately 798 K. Thus, any measurements above this temperature on Te-rich samples were not included in this study. Schenk et al. circumvented this problem by calculating the carrier concentration *in situ* at higher temperatures [18]. Their numbers are orders of magnitude higher than the ones previously reported and have not been replicated, therefore, we have chosen not to include them during the optimization.

Carrier concentration experiments are useful in determining the number of defects in a material; however, they give no insight into the nature of the defects. Measurements of the effect of partial pressure on the carrier concentration have been used in the past to provide insight into the type of defects in a system [19]. However, first-principle calculations can now provide us with the energies of formation of a multitude of different charged and neutral defects within the system. Recent studies by Doak et al. and Bajaj et al. have determined that the lowest formation energy under Te-rich and Pb-rich conditions are doubly charged Pb and Te vacancies, respectively [8] [20]. These calculations are based on the dilute-limit approximation, where formation energies are determined by energy differences in defect containing and defect-free supercells. Care has to be taken when dealing with charged defects in first-principle calculations due to the long-range electrostatic interactions that arise in periodic boundary conditions. Both studies use similar correction terms to address this issue. Their final values for formation energies vary (i.e. the formation energy of a doubly-ionized Pb vacancy in Te-rich conditions are 0.35 and 0.53 eV/atom for [8] and [20], respectively), however, are in qualitative agreement. These calculations could be improved with the use of spin-orbit coupling to better describe the experimental band-gap, but are computationally expensive on supercells of these sizes. To be consistent between PbTe and PbS, this study will use values from Doak et al, as it contains information on both the PbS and PbTe system. Therefore, our model uses these defects as the predominant ones. Similar choices have been made for non-CALPHAD models with success [21].

2.2 Pb-S

The Pb-S system has been studied very similarly to the Pb-Te system. Most studies involve single crystals annealed at high temperature in either Pb-rich or S-rich environments, followed by a quench, and subsequent Hall measurements. The results by Bloem and Kroger, Nensberg and Petrov, and Chou et al. are all in close agreement. [22] [23] [24]. However, similar to the PbTe system, Albers et al. determined that Bloem and Kroger were not able to maintain the equilibrium concentration of PbS above 973 K when quenching. Therefore, we did not include their data, along with Nensberg and Petrov, and Chou et al. as they are all in close agreement and therefore equally questionable. No data points below 973 K are provided for either study and therefore, cannot be used.

Strauss calculated the carrier concentration of n-type PbS by quenching Bridgman-grown single crystals [25]. Their data is in disagreement with the previously mentioned Nensberg and Petrov and Bloem and Kroger data, which was attributed to the latter's unsuccessful quench and incorrect anneal times. Data from Strauss was used in a later study by Harman, who supplemented it with p-type data below 973 K [14]. These two experiments are used to optimize the parameters for the PbS semiconductor models.

PbS also has very similar defect chemistry to PbTe. Again, first-principle calculations have shown that doubly charged vacancies in PbS exhibit the lowest formation energies in the system [20] [26] [27]. In addition, the doubly charged vacancies have been used previously in other models with success [28] and therefore will be used for modeling the defects in PbS.

3. CALPHAD Model

3.1 5-Sublattice Model

The CALPHAD method has been used several times to describe the Pb-Te system, notably by Kattner et al. [29] and even more recently by Gierlotka et al. [30], and Bajaj et al. [8]. The crystal structure of PbS and PbTe are both NaCl B1 [31], which is generally modeled using two sublattices, one for each atomic site. Gierlotka modeled PbTe using a two sublattice anti-site model. First-principle calculations indicate this to likely not be the most accurate model, as formation energies for antisite defects are larger than vacancies. This was improved in Bajaj's assessment, which correctly placed vacancies on either sublattice. The stoichiometric PbTe and associate liquid models show excellent agreement between the description and experimental information, therefore we chose to use Bajaj's description of the liquid and stoichiometric PbTe in our own optimization. The full phase diagram of the Pb-Te system is shown in Figure 1. The Pb-S system has not been so thoroughly investigated via the CALPHAD method. A recent assessment by Huang et al. is the only CALPHAD study of note, however, it models PbS as a stoichiometric compound [9]. This phase diagram is shown in Figure 2.

Figure 1: Full Pb-Te Phase Diagram taken from Bajaj 's assessment [8]

Figure 2: Full Pb-S Phase Diagram taken from Huang's assessment [9]

The goal of this study is to implement the five-sublattice model for semiconductors developed by Chen et al. for PbTe and PbS [32]. The five-sublattice model uses the Wagner-Schottky defect model and compound energy formalism (CEF) to better describe carrier concentration and defect energies. The model has its roots in the species chemical potential/bond energy (SCPBE) model developed by Oates et al. [33]. Chen transformed that model into the CEF formulism, which can be easily implemented in programs such as ThermoCalc. Chen then used this model to successfully model the semiconductor compounds GaAs as well as CdTe [10] [32]. It has also been used for the GaN semiconductor [34] and recently for ZnO [35].

The five sublattice model for the PbX ($\text{X}=\text{S}, \text{Te}$) is given as: $(\text{Pb}, \text{Va}, \text{Va}^{-2})(\text{X}, \text{Va}, \text{Va}^{+2})(\text{Va})(\text{Va}, \text{e}^{-1})(\text{Va}, \text{h}^{+1})$, where the first, second, third, fourth, and fifth sublattices are for the Pb, X, interstitial, electrons, and holes respectively. Mathematically the CEF is given below:

$$G^{\text{PbX}} = \sum_i \sum_j \sum_k \sum_l \sum_m y_i^{\text{Pb}} y_j^{\text{X}} y_k^{\text{I}} y_l^{\text{e}} y_m^{\text{h}} G_{ijklm} + \text{RT} \left(\sum_i y_i^{\text{Pb}} \ln y_i^{\text{Pb}} + \sum_j y_j^{\text{X}} \ln y_j^{\text{X}} + \sum_k y_k^{\text{I}} \ln y_k^{\text{I}} + \sum_l y_l^{\text{e}} \ln y_l^{\text{e}} + \sum_m y_m^{\text{h}} \ln y_m^{\text{h}} \right) \quad (1)$$

Where y_i^s represents the site fraction of i on sublattice s , R is the gas constant, and T is temperature. The interstitial sublattice will not be used in this study, but is kept for completeness and for possible ternary extrapolations. The introduction of charged species within this model add an additional constraint when the Gibbs free energy is minimized. In addition to the usual requirement that the total amount of components is constant and that all site fractions sum to one for individual sublattices, all phases must be electrically neutral. With five sublattices, the number of end-members in this model becomes 36, however, Chen et al. describe how to reduce the number of optimized end-members, which will be given below.

The creation of an electron and hole pair is given by [10]:

$${}^0G_{PbXVa e^{-1}Va} + {}^0G_{PbXVaVa h^{+1}} = 2 {}^0G_{PbXVaVaVa} + E_g - RT(\ln N_c + \ln N_v) \quad (2)$$

E_g is the band gap energy of PbX, $G_{PbXVaVaVa}$ are taken from the stoichiometric descriptions in Bajaj and Huang's assessments, and N_c and N_v are the effective density of states for non-degenerate semiconductors given by:

$$N_{c,v} = 2 \left(\frac{2\pi m_{c,v}^* kT}{h^2} \right)^{3/2} \left(\frac{a^3}{4} \right) \quad (3)$$

where $m_{c,v}^*$, k , h , and a are the effective masses of the electron and holes, Boltzmann constant, and lattice parameters respectively. The parameters for PbX used in these equations are given in Table 1. E_g is temperature dependent for PbX and increases with temperature. However, there is limited data on the high temperature dependence. The band gap plateaus above 500 K, therefore, the band gap at 500 K is used here as a constant at higher temperatures [31]. A reference state for the energy levels of the charge carriers must be chosen. Due to the non-degenerate behavior of these semi-conductors, the middle of the band gap, where the assumed Fermi energy is an appropriate choice and one used by convention in previous assessments using this model [10] [32] [33] [35]. Using this reference, the Gibbs free energy for the end members containing electrons and holes can be determined using Equation 2 [32]:

$${}^0G_{PbXVa e^{-1}Va} = {}^0G_{PbXVaVaVa} + \frac{E_g}{2} - RT \ln N_c \quad (4)$$

$${}^0G_{PbXVaVa h^{+1}} = {}^0G_{PbXVaVaVa} + \frac{E_g}{2} - RT \ln N_v \quad (5)$$

Charged defects are modeled with respect to their neutral end-member defects as well as the creation of their respective charge carrier and ionization energies. Since doubly charged vacancies are the dominant defects in the system, each charged defect end-member creates two charge carriers and are calculated as [32]:

$${}^0G_{Va^{-2}XVaVaVa} = {}^0G_{VaXVaVaVa} - 2 {}^0G_{PbXVaVa h^{+1}} + 2 {}^0G_{PbXVaVaVa} + \Delta E_{V_{Pb}^{-2}} \quad (6)$$

$${}^0G_{PbVa^{+2}VaVaVa} = {}^0G_{PbVaVaVaVa} - 2 {}^0G_{PbXVa e^{-1}Va} + 2 {}^0G_{PbXVaVaVa} + \Delta E_{V_X^{+2}} \quad (7)$$

The values $\Delta E_{V_{Pb}^{-2}}$ and $\Delta E_{V_X^{+2}}$ represent the ionization energies or defect transition energies of vacancies on the Pb and X sublattice with respect to the valence and conduction band, respectively. The transition energies used are those determined at 0 K by first-principle calculations and are assumed to be constant at higher temperature. These energies are calculated by determining the chemical potential of an electron at which the formation energy of the neutral defect and charged defect are equal to one another [36]. In the PbX system, the transition of importance is between that of the neutral vacancy and its charge state of ± 2 . The ionization energies can therefore be calculated from the given energies in [20] and the values are summarized in Table 1. Due to the discrepancy between the

experimental and DFT calculated band gaps, these chemical potentials have been scaled by the ratio of their respective DFT values.

$$\frac{\mu_{e,DFT}}{E_{g,DFT}} = \frac{\mu_{e,exp}}{E_{g,exp}} \quad (8)$$

Therefore, we can determine the experimental chemical potential at which ionization occurs by solving for $\mu_{e,exp}$ in Equation 8 above.

Table 1: Physical parameters used in the five-sublattice model for PbX (X=S,Te) semiconductors

Model Parameter	PbTe	PbS
E_g (ev)	0.360 ^a	0.472 ^a
m_e^*	0.30 m_0^b	0.39 m_0^c
m_h^*	0.36 m_0^b	0.38 m_0^d
a (nm)	0.6462 ^a	0.5936 ^a
$\Delta E_{V_{Pb}^{-2}}$ (ev/defect)	-0.011	-0.097
$\Delta E_{V_X^{+2}}$ (ev/defect)	0.19	0.18
a) [31] ^b [37] ^c [3] ^d [38]		

The reciprocal relation, utilized commonly in CALPHAD assessments, is used to calculate end-members that contain two defects on the first two sublattices. Due to the large amount of end-members without physical meaning, no experimental information, and to not introduce a miscibility gap, we assume the reciprocal energy is equal to zero [5] and the end-members are calculated as:

$${}^0G_{ijVaVaVa} = {}^0G_{iXVaVaVa} + {}^0G_{PbJVaVaVa} - {}^0G_{PbXVaVaVa} \quad (9)$$

End-members with three or more defects are set equal to 0. This is a safe assumption to make, as these end-members will have very small contributions to the total Gibbs free energy, due to the small amount of site fractions of the constituents on sublattices. Therefore, the pre-factor in Equation 1 of these end-members will be near zero and therefore any reasonable number can be used.

There are only two remaining end members that require optimization, which represent the neutral defects on the first two sublattices. They are given as:

$${}^0G_{PbVaVaVaVa} = {}^0G_{Pb}^{fcc} + V_1 + V_2T \quad (10)$$

$${}^0G_{VaXVaVaVa} = {}^0G_X^{SER} + V_3 + V_4T \quad (11)$$

where the functions ${}^0G_i^{SER}$ are the Gibbs free energies in their standard elemental reference state given by Dinsdale [39]. The variables V_1 to V_4 are the optimizing parameters used to fit to the experimental data.

3.2 2SL Model

The 5SL model remains interesting from a scientific perspective as it contains many of the physical parameters used in semiconductors physics. The model is based on the grand-canonical approach, which is the preferred method for calculating defects in binary and ternary systems [40]. However, it has limited capability for developing a multicomponent database as the structure-based end-members are optimized from system specific information. Therefore, there is incompatibility between the end-member ${}^0G_{PbVaVaVaVa}$ in the PbTe and PbS systems. To address this, a two-sublattice (2SL) model will be developed that is compatible in multi-component databases.

The 2SL model is described as (Pb,Va)(X,Va) and due to the vacancies, great care needs to go into determining the end-members and interaction parameters [40]. The PbX system can be split into two regions by the stoichiometric composition. Along the Pb-rich solidus, the site fraction of X vacancies will be orders of magnitude larger than Pb vacancies and as such can be assumed to be equivalent to the model (Pb)(X,Va). This reduces the degrees of freedom to one: the site fraction of vacancies or X atoms on the X sublattice. To determine the equilibrium concentration of Te the grand potential must be minimized:

$$\mathcal{G}_m = G_m - \mu_{Pb}y_{Pb} - \mu_X y_X \quad (12)$$

where $\mathcal{G}_m$, μ_{Pb} and μ_{Te} are the grand potential per mole and chemical potential of Pb and Te atoms respectively. According to the CEF, G_m with only one excess term is calculated as

$$G_m = y_X {}^0G_{PbX} + y_{Va} {}^0G_{PbVa} + RT(y_X \ln(y_X) + y_{Va} \ln(y_{Va})) + y_X y_{Va} L_{X,Va} \quad (13)$$

Taking the derivative of Equation $\mathcal{G}_m = G_m - \mu_{Pb}y_{Pb} - \mu_X y_X$ (12 with respect to y_X and since μ_X is constant in the two-phase region, and setting the result to zero leads to

$$0 = \frac{d\mathcal{G}_m}{dy_X} - \mu_X \quad (14)$$

Taking the derivative of Equation $G_m = y_X {}^0G_{PbX} + y_{Va} {}^0G_{PbVa} + RT(y_X \ln(y_X) + y_{Va} \ln(y_{Va})) + y_X y_{Va} L_{X,Va}$ (13 with respect to y_X and substituting into Equation $0 = \frac{d\mathcal{G}_m}{dy_X} - \mu_X$ (14 leads to

$$- {}^0G_{PbVa} + {}^0G_{PbX} + L_{X,Va}(1 - 2y_X) - \mu_X = RT \ln\left(\frac{y_X}{1-y_X}\right) \quad (15)$$

Finally, the equilibrium concentration of vacancies can be determined by substituting $1 - y_{Va}$ for y_X and assuming a dilute concentration, where $y_{Va} \ll 1$

$$y_{VaX}^{eq} = \exp\left(-\frac{{}^0G_{PbVa} - {}^0G_{PbX} + L_{X,Va} + \mu_X}{RT}\right) \quad (16)$$

The numerator in Equation $y_{VaX}^{eq} = \exp\left(-\frac{{}^0G_{PbVa} - {}^0G_{PbX} + L_{X,Va} + \mu_X}{RT}\right)$ (16 represents the formation energy of a vacancy per mole, which can be determined from first-principle

calculations. The key advantage of this is that the formation energy is split into a structure specific term $^{\circ}G_{PbVa}$, which can be used in all PbX systems, and a system specific term $L_{X,Va}$ which can be changed to fit the first-principle or experimental data unique to the system. The chemical potential of μ_X is fixed in a two-phase region at a given temperature. Therefore, once a value for $^{\circ}G_{PbVa}$ is agreed upon, only the interaction parameter must be adjusted. A similar analysis for X-rich conditions determines the equilibrium site fraction of Pb vacancies as

$$y_{VaPb}^{eq} = \exp\left(-\frac{^{\circ}G_{VaX} - ^{\circ}G_{PbX} + L_{Pb,Va} + \mu_{Pb}}{RT}\right) \quad (17)$$

The modeling of end-members containing vacancies is a known issue that has been frequently discussed [40] [41] [42]. First attempts at modeling end-members containing vacancies assigned them values of zero, which can cause them to stabilize at extremely high temperatures [42]. To fix this, a positive and generally temperature dependent, value must be used for modeling vacancies. Rogal's review article suggests using a value of $2.3RT$ as a penalty value. This value was chosen as a method for making sure that the concentration of vacancies on a sublattice would not exceed 0.1 at which point the crystal would likely collapse. Dinsdale recently recommended a value of $30T$ for convenience, as it is both positive and increasing with temperature [42]. Franke analyzed the concentration of vacancies in tungsten and determined that the description needed to exceed the value of $\ln(2 - 1/2)RT$ for there to be a unique solution for the vacancy concentration [41]. His final recommendation is a value of $0.2RT$. For this study, the Gibbs free energy of Pb or X in their standard elemental reference state and the value of $2.3RT$ is chosen for end-members containing vacancies due to the reasonable assumption that the site fraction should not exceed 0.1 and to ensure that PbX does not become stable on the Pb or X end of the phase diagram. This avoids a not physically relevant order/disorder model between PbX and FCC_A1, similar to the one between BCC_A2 and the B2 phase in the Al-Ni system [43], as PbX is not formed through a second order phase transition.

The defect containing end-members for the 2SL model are then given as:

$$^{\circ}G_{PbVa} = ^{\circ}G_{Pb}^{fcc} + 2.3RT \quad (18)$$

$$^{\circ}G_{VaX} = ^{\circ}G_X^{SER} + 2.3RT \quad (19)$$

$$^{\circ}G_{VaVa} = 4.6RT \quad (20)$$

and the interaction parameters can be linked to the energy of formation through Equation

$$y_{VaX}^{eq} = \exp\left(-\frac{^{\circ}G_{PbVa} - ^{\circ}G_{PbX} + L_{X,Va} + \mu_X}{RT}\right) \quad (16 \text{ and } y_{VaPb}^{eq} = \exp\left(-\frac{^{\circ}G_{VaX} - ^{\circ}G_{PbX} + L_{Pb,Va} + \mu_{Pb}}{RT}\right) \quad (17:$$

$$L_{Pb,Va} = G_{VaPb}^f - ^{\circ}G_{VaX} + ^{\circ}G_{PbX} - \mu_{Pb} \quad (21)$$

$$L_{X,Va} = G_{VaX}^f - ^{\circ}G_{PbVa} + ^{\circ}G_{PbX} - \mu_X \quad (22)$$

The interaction parameters are given start values based off the first-principle calculations for the energies of formation and are allowed to vary to fit the experimental data. In this model, the assumption is made that for every Pb vacancy two holes are created. Likewise, every Te vacancy results in the creation of two electrons.

4. Results and Discussion

The PARROT [40] module in ThermoCalc [41] was used to optimize the parameters V_1 to V_4 for PbTe and PbS. The temperature independent terms V_1 and V_3 represent the formation energy of the neutral vacancies on the X and Pb sites, respectively. These values were provided from the authors of [20] as they were calculated in their recent study, but are not explicitly given in the paper due to their high formation energy compared to the other defects. Values for these calculations are found in Table 2. Optimizations that converged far from these values were deemed inaccurate and not used. The experimental carrier concentrations previously discussed were then used to fit the parameters.

4.1 PbTe

The final optimized end-members for PbTe are given in Table 2 along with the initial values calculated from first-principles at 0 K. The carrier concentration of holes and electrons in PbTe along with the experimental data is given in Figure 3 and Figure 4, respectively. For comparison, the recent assessment by Bajaj, assuming that each Pb and Te vacancy creates 2 holes and electrons, respectively, is also provided. In each case, the new five-sublattice model has a much better fit to the data.

Table 2: Final optimization end-members for PbTe and PbS semiconductors. The first-principle calculations are used as starting values for the temperature independent term in the Gibbs free energy and are taken from a recent study [20]. All units J/mol.

End-Member	Optimized End-Member	First-principle Calculation
PbTe		
${}^0G_{\text{PbVaVaVaVa}}$	${}^0G_{\text{Pb}}^{fcc} + 143,576 + 62.8T$	127,000
${}^0G_{\text{VaTeVaVaVa}}$	${}^0G_{\text{Te}}^{hex} + 98,408 + 79.2T$	115,000
PbS		
${}^0G_{\text{PbVaVaVaVa}}$	${}^0G_{\text{Pb}}^{fcc} + 92,724 + 75.2T$	96,000
${}^0G_{\text{VaSVaVaVa}}$	${}^0G_{\text{S}}^{orth} + 112,427 + 82.7T$	83,900

Table 3: Final optimized interaction parameters for the PbX system. Using Equation $L_{\text{Pb,Va}} = G_{\text{VaPb}}^f - {}^0G_{\text{VaX}} + {}^0G_{\text{PbX}} - \mu_{\text{Pb}}$ (21 and $L_{\text{X,Va}} = G_{\text{VaX}}^f - {}^0G_{\text{PbVa}} + {}^0G_{\text{PbX}} - \mu_{\text{X}}$ (22, the formation energy can be calculated and compared to the DFT value. These parameters coupled with Equations ${}^0G_{\text{PbVa}} = {}^0G_{\text{Pb}}^{fcc} + 2.3RT$ (18 to ${}^0G_{\text{VaVa}} = 4.6RT$ (20 are used for modeling PbX.

Interaction Parameter	Optimized Value (J/mol)	CALPHAD Determined	DFT Predicted Formation Energy
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		Formation Energy at 300 K (J/mol)	at 300 K (J/mol) [20]
$L_{Pb,Va:Te}$	$38,070+2.4T$	44,500	51,100
$L_{Pb:Te,Va}$	$72,780-10.8T$	75,300	82,900
$L_{Pb,Va:S}$	$38,570+4.4T$	40,400	36,600
$L_{Pb:S,Va}$	$38,944+4.6T$	46,100	75,100

The carrier concentration of holes and electrons (p and n) can be converted to solidus points via the equation [42] [43]:

$$X_m = 0.5 + \frac{(p-n)M_{PbX}}{4Z\rho N_A} \quad (23)$$

where M_{PbX} is the molecular weight of PbX , Z is the ionization of the defect, in this case 2, ρ is the density, and N_A Avogadro's number. Using this formula, the data has been converted to solubility limits and the off-stoichiometric nature of $PbTe$ is shown in Figure 5.

Figure 3: Carrier concentration of holes under Te-rich conditions and experimental data points for $PbTe$. Data points above 800 K were not used in this assessment. Bajaj's assessment shown as green line, the 5SL in black and the 2SL model shown in magenta. The dashed magenta line shows the same calculation with the liquid phase suspended and shows much better agreement with the high temperature data.

Figure 4: Carrier concentration of electrons under Pb-rich conditions and experimental data points for PbTe. Bajaj's assessment shown as green line, 5SL in black, and the 2SL model shown in magenta.

Figure 5: Enlarged region of Pb-Te phase diagram to show solubility of PbTe. Data points above 800 K on the Te-rich side were not used in this assessment. Bajaj assessment shown as green line, the 5SL in black, and the 2SL model shown in magenta.

A second model of PbTe was also used in this assessment that contained Te^0 and Te^{+2} antisite defects on the Pb sublattice. This was investigated due to the formation energy of the Te^{+2} defect energy (0.90 eV/defect) being only slightly larger in the Te-rich region than the doubly charged vacancy on the Te sublattice under Pb-rich conditions (0.85 eV/defect) [20]. However, attempts to fit this model led to unphysical end-members that did not describe the data as well. Therefore, we have decided to only include vacancies in this model. Although the enthalpies of formation at 300 K are similar for Te^{+2} and Va^{-2} on the Pb-sublattice and Te-sublattice, respectively, they are only comparable under opposing growth conditions. If the Te^{+2} antisite defects are calculated under the same equilibrium as $\text{Va}_{\text{Te}}^{+2}$, Pb-rich, then the enthalpy of formation rises dramatically from 0.90 eV/defect to

2.79 eV/defect. On the Te-rich side, the formation energy is 0.90 eV/defect, which is much higher than the V_{Pb}^{-2} at 0.53 eV/defect and therefore plays a minor role. The comparison between the two defects is even greater in Bajaj's calculation where the difference is 0.35 and 0.87 eV/defect [8]. The differences in formation energy between the V_{Pb}^{-2} and $\text{Te}_{\text{Pb}}^{+2}$ defect in Te-rich conditions results in over an order of magnitude difference between the concentrations of the two defects at 1000 K [20]. This difference is within the experimental error of the measurements with which the parameters of the models are fit to and therefore cannot be used to reliably determine these values.

The five-sublattice model describes the experimental information quite well, however, there are important assumptions made that could be improved. Mainly, recent work has shown that PbTe has a non-parabolic band structure [44] and at high temperatures could be a degenerate semiconductor [20]. This model assumes both parabolicity and non-degeneracy, which allows us to describe the density of states using Maxwell-Boltzmann statistics, thereby greatly simplifying the calculations. Other attempts to model PbTe have faced the same problem and have come to the conclusion that these assumptions are still reasonable [21]. Although these assumptions hold well for intrinsic PbTe these semiconducting materials are useful when doped with a third element, which will most certainly raise the carrier concentration and make the semiconductor degenerate. Therefore, future work is needed to develop a semiconductor model that does not require these assumptions.

The 2SL model is shown in magenta in Figure 3-Figure 5. At low temperatures, the 2SL model describes the data quite well and closely resembles the 5SL model. At higher temperatures, particularly when the solid is in equilibrium with the liquid, it begins to deviate. This is not seen in the PbS system shown below. Attempts to reoptimize the liquid parameters with the carrier concentration did not improve the high temperature data, neither did introducing more interaction parameters. An interaction parameter that changes at the eutectic temperature would improve the description, but there is little physical justification for it. Calculations with the liquid phase suspended, shown as the dashed line, on the Te-rich side show better agreement with the experimental data at higher temperature. It is clear that the liquid phase plays a large role in determining the equilibrium carrier concentration. Despite the discrepancy in the experimental data at higher temperature, the interaction parameters agree well with the values determined from first-principle calculations at 300 K and agree well below the eutectic point.

4.2 PbS

The final optimized end-members for PbS are given in Table 2 as well. Similar to PbTe, the final end-members do not deviate far from the first-principle calculations. The carrier concentration of holes and electrons are given in Figure 6 and Figure 7, respectively. A satisfactory fit between the model and the experiment is shown. There are no previous CALPHAD assessments that do not treat PbS as a stoichiometric compound; therefore, no other fits are shown. Again, the carrier concentration data can be converted to solidus lines and the off-stoichiometric nature of PbS is given in Figure 8.

Similar to PbTe, a second model for PbS was also investigated. From the first-principle calculations, a single ionized vacancy on the S site had a slightly larger formation energy than the doubly ionized vacancy [20]. However, when optimizing with this model,

the concentration of V_S^{+1} was sufficiently small enough that we removed it from the model without any loss of accuracy. In addition, PbS is also a non-parabolic semiconductor and will also become degenerate when doped with a third element. Therefore, a new model will be necessary in the future to take these properties into account.

The 2SL model for PbS shows remarkable agreement with the experimental data and 5SL model. In the carrier concentration plots, the two are nearly indistinguishable and only deviate in the phase diagram at high temperatures where the concentration is linearly dependent on the carrier concentration. The formation energies based on the interaction parameters are also in qualitative agreement with the first-principle calculations in that the Pb vacancy is lower in energy than an S vacancy.

Figure 6: Carrier Concentration of holes under S-rich conditions and experimental data points. The 5SL model is shown in black and the 2SL model is shown in magenta.

Figure 7: Carrier Concentration of electrons under Pb-rich conditions and experimental data points. The 5SL model is shown in black and the 2SL model is shown in magenta.

Figure 8: Enlarged region of Pb-S phase diagram to show solubility of PbS. The 5SL model is shown in black and the 2SL model is shown in magenta.

5. Conclusion

This study has developed new model descriptions for the binary PbTe and PbS semiconductors. The model is different than previous ones used as it explicitly has sublattices dedicated to electrons and holes. An excellent fit to the carrier and phase boundaries has been found for both systems. The PbTe free energies show a marked improvement from previous models and the PbS is new and consistent with the experimental and first-principles data. The carrier concentration has been converted into solubility data and new phase diagrams have been developed. First-principles calculations were used to provide starting values for the assessment to make the models more physically accurate. The 5SL model could be improved by explicitly incorporating the band structure of the semiconductors, but the parabolic band assumption has been proved to be sufficient to describe the data. In addition, a 2SL model compatible in multicomponent databases has also been determined. Using a fixed value of $2.3RT$ for vacancy containing end-members, the model can then be fit to the experimental data. In addition, the interaction parameter can be linked to the formation energy for further physical significance. The 2SL model shows good agreement with the experimental data, particularly in the PbS system and qualitatively agrees with the first-principle calculations. These models can be used to optimize the properties of TE devices where phase equilibrium play a key role in their already high ZT values.

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References

- [1] Francis DiSalvo, "Thermoelectric Cooling and Power Generation," *Science*, vol. 285, pp. 703-706, 1999.
- [2] Joseph Heremans, Christopher Thrush, and Donald Morelli, "Thermopower enhancement in lead telluride nanostructures," *Physical Review B*, vol. 70, p. 115334, 2004.
- [3] Heng Wang, Eugen Schechtel, Yanzhong Pei, and Jeffrey Snyder, "High Thermoelectric Efficiency of n-type PbS," *Advanced Energy Materials*, vol. 3, pp. 488-495, 2013.
- [4] John Androulakis et al., "Spinodal Decomposition and Nucleation and Growth as a Means to Bulk Nanostructured Thermoelectrics: Enhanced Performance in Pb_{1-x}Sn_xTe-PbS," *Journal of American Chemical Society*, vol. 129, pp. 9780-9788, 2007.
- [5] Hans Lukas, Suzana Fries, and Bo Sundman, *Computational Thermodynamics: The CALPHAD Method*. Cambridge: Cambridge University Press, 2007.
- [6] National Research Council, "Integrated Computational Materials Engineering: A transformational Discipline for Improved Competitiveness and National Security," *The National Academies Press*, 2001.
- [7] Zi-Kui Liu, "First-Principles Calculations and CALPHAD Modeling of Thermodynamics," *Journal of Phase Equilibria and Diffusion*, vol. 30, pp. 517-534, 2009.
- [8] Saurabh Bajaj et al., "Ab initio study of intrinsic point defects in PbTe: an insight into phase stability," *Acta Materialia*, vol. 92, pp. 72-80, 2015.
- [9] Shenming Huang, Yajun Liu, Yang Chen, and Zhitao Kang, "Thermodynamic Descriptions and Phase Diagrams for Pb-S and Bi-S Binary Systems," *Journal of Electronic Materials*, vol. 43, pp. 1237-1243, 2014.
- [10] Qing Chen and Mats Hillert, "The compound energy model for compound semiconductors," *Journal of Alloys and Compounds*, vol. 245, pp. 125-131, 1996.
- [11] R.F. Brebrick and R.S. Allgaier, "Composition Limits of Stability of PbTe," *The Journal of Chemical Physics*, vol. 32, pp. 1826-1831, 1960.
- [12] R.F. Brebrick and E. Gubner, "Composition Stability Limits of PbTe. II," *The Journal of Chemical Physics*, vol. 36, pp. 1283-1289, 1962.
- [13] W.W. Scanlon, "Precipitation of Te and Pb in PbTe Crystals," *Physical Review*, vol. 126, pp. 509-513, 1962.
- [14] T.C. Harman, "Control of Imperfections in Crystals of Pb_{1-x}Sn_xTe, Pb_{1-x}Sn_xSe, and PbS_{1-x}Se_x," *Journal of Nonmetals*, vol. 1, pp. 183-194, 1973.
- [15] Robert Hewes, Michael Adler, and Stephen Senturia, "Annealing studies of PbTe and Pb_{1-x}Sn_xTe," *Journal of Applied Physics*, vol. 44, pp. 1327-1332, 1973.
- [16] W. Albers, C. Haas, and H.J. Vink, *Phillips Res. Rep.*, vol. 18, p. 372, 1963.
- [17] M Muhlberg and D. Hesse, "TEM Precipitation Studies in Te-Rich As-Grown PbTe Single Crystals," *Physica status solidi*, vol. 76, pp. 513-524, 1983.
- [18] M. Schenk, H. Berger, A. Klimakow, M. Muhlberg, and M. Wienecke, "Nonstoichiometry and Point Defects in PbTe," *Cryst. Res. Technol.*, vol. 1, pp. 77-84, 1988.
- [19] F.A. Kroger and H.J. Vink, "Relations between the concentration of imperfections in

- solids," *Journal of Physical Chemistry Solids*, vol. 5, pp. 208-223, 1958.
- [20] Jeff Doak, Kyle Michel, and Chris Wolverton, "Determining dilute-limit solvus boundaries in multi-component systems using defect energetics: Na in PbTe and PbS," *Journal of Materials Chemistry C*, vol. 3, no. 40, pp. 10630-10649, 2015.
- [21] Yi Sha and Robert Brebrick, "Explicit Incorporation of the Energy-Band Structure into an Analysis of the Defect Chemistry of PbTe and SnTe," *Journal of Electronic Materials*, vol. 18, pp. 421-443, 1989.
- [22] J. Bloem and F.A. Kroger, "The P-T-X Phase Diagram of the Lead-Sulfur System," *Z. Phys. Chem*, vol. 7, pp. 1-14, 1956.
- [23] Y. Nensberg and A. Petrov, "Thermally Generated Charge Carriers in PbS," *Inorganic Material*, vol. 1, p. 1365, 1965.
- [24] N. Chou, K. Komarek, and E. Miller, "Retrograde Solubility of Pbs, PbSe, and PbTe," *Transactions of the Metallurgical Society of AIME*, vol. 245, pp. 1553-1560, 1969.
- [25] A.J. Strauss, "Retrograde Solubility of Lead in n-Type PbS," *Transactions of the Metallurgical Society of AIME*, vol. 239, pp. 794-798, 1967.
- [26] Aron Walsh, "Defect Processes in a PbS Metal Organic Framework: A Quantum-Confined Hybrid Semiconductor," *The Journal of Physical Chemistry Letters*, vol. 1, pp. 1284-1287, 2010.
- [27] Wun-Fan Li, Chang-Ming Fang, Marjolein Kijkstra, and Marjin A van Huis, "The role of point defects in PbS, PbSe and PbTe: a first principles study," *Journal of Physics: Condensed Matter*, vol. 27, p. 355801, 2015.
- [28] R.C. Sharma, J.C. Lin, and Y.A. Chang, "A Thermodynamic Analysis of the Pb-S System and Calculation of the Pb-S Phase Diagram," *Metallurgical Transactions B*, vol. 18B, pp. 237-244.
- [29] U. Kattner, H.L. Luaks, and G. Petzow, "Optimization and calculation of the Pb-Te System," *CALPHAD*, vol. 10, pp. 103-116, 1986.
- [30] Wojciech Gierlotka, Joanna Lapsa, and Dominika Jendrzeyczyk-Handzlik, "Thermodynamic description of the Pb-Te system using ionic liquid model," *Journal of Alloys and Compounds*, vol. 479, pp. 152-156, 2009.
- [31] Otfried Madelung, *Semiconductors: Data Handbook*.: Springer-Verlag Berlin Heidelberg, 2004.
- [32] Q. Chen et al., "Phase Equilibria, Defect Chemistry and Semiconducting Properties of CdTe(s) - Thermodynamic Modeling," *Journal of Electronic Materials*, vol. 27, pp. 961-971, 1998.
- [33] W.A. Oates, G. Eriksson, and H. Wenzl, "Thermodynamic modelling of solid gallium arsenide," *Journal of Alloys and Compounds*, vol. 220, pp. 48-52, 1995.
- [34] Jing-Bo Li and Jean-Claude Tedenac, "Thermodynamic Modeling of Native Point Defects and Dopants of GaN Semiconductors," *Journal of Electronic Materials*, vol. 31, pp. 321-326, 2002.
- [35] Jingbo Li and Lei Kerr, "Thermodynamic modeling of native defects in ZnO," *Optical Materials*, vol. 35, pp. 1213-1217, 2013.
- [36] A. F. Kohan, G. Ceder, D. Morgan, and C. Van de Walle, "First-principles study of native

- point defects in ZnO," *Physical Review B*, vol. 61, p. 15019, 2000.
- [37] Yanzhong Pei, Aaron LaLonde, Shiho Iwanaga, and Jeffrey Snyder, "High thermoelectric figure of merit in heavy hole dominated PbTe," *Energy & Environmental Science*, vol. 4, p. 2085, 2011.
 - [38] Li-Dong Zhao et al., "Thermoelectrics with Earth Abundant Elements: High Performance p- type PbS Nanostructured with SrS and CaS ," *Journal of the American Chemical Society*, vol. 134, p. 7902, 2012.
 - [39] A.T. Dinsdale, *CALPHAD*, vol. 15, pp. 317-425, 1991.
 - [40] B. Jansson, "Ph.D. Thesis," *Royal Institute of Technology, Stockhol, Sweden*, 1984.
 - [41] B Sundman, B. Jansson, and J.O. Andersson, *CALPHAD*, vol. 9, p. 149, 1985.
 - [42] J.C. Lin, K.C Hsieh, R.C. Sharma, and Y.A. Chang, "The Pb-Te (Lead-Tellurium) System," *Bulletin of Alloy Phase Diagrams*, vol. 10, pp. 340-347, 1989.
 - [43] J.C. Lin, R.C. Sharma, and Y.A. Chang, "The Pb-S (Lead-Sulfur) System," *Bulletin of Alloy Phase Diagrams*, vol. 7, pp. 374-381, 1986.
 - [44] Yanzhong Pei et al., "Optimum Carrier Concentration in n-Type PbTe Thermoelectrics ," *Advanced Energy Materials*, vol. 4, p. 1400486, 2014.
 - [45] Zachary Gibbs et al., "Temperature dependent band gap in PbX (X=S, Se, Te)," *Applied Physics Letters*, vol. 103, p. 262109, 2013.
 - [46] B.J. Sealy and A.J. Crocker, "The P-T-x phase diagram of PbTe and PbSe," *Journal of Materials Science* , vol. 8, pp. 1737-1743, 1973.
 - [47] A.J. Strauss, "Effect of Pb and Te Saturation on Carrier Concentrations in impurity-doped PbTe," *Journal of Electronic Materials*, vol. 4, pp. 553-569, 1973.
 - [48] T Ngai, R.C. Sharma, and Y.A. Chang, "Thermodynamic Properties and Phase Equilibria of the Lead-Tellurium Binary System," *Monatshefte fur Chemie*, vol. 118, pp. 277-300, 1987.
 - [49] R.F Brebrick, "Analysis of the Solidus Lines for PbTe and SnTe," *Journal of Electronic Materials*, vol. 6, pp. 659-692, 1977.
 - [50] Masatomo Fujimoto and Yasuo Sato, "P-T-x Phase Diagram of the Lead Telluride System," *Japanese Journal of Applied Physics*, vol. 5, pp. 128-133, 1966.
 - [51] Simon Johnsen et al., "Nanostructures Boost the Thermoelectric Performance of PbS ," *Journal of The American Chemical Society*, vol. 133, pp. 3460-3470, 2011.
 - [52] E. Miller and K.L. Komarek, "Retrograde Solubility in Semiconducting Intermetallic Compounds. Liquidus Curves in the Pb-S, Pb-Se, and Pb-Te Systems," *Transactions of the Metallurgical Society of AIME*, vol. 236, pp. 832-840, 1966.
 - [53] T.C. Harman and A.J. Strauss, "Preparation and Properties of PbS Crystals with Low Carrier Concentration," *Journal of Electronic Materials*, vol. 5, pp. 621-644, 1976.
 - [54] Aaron LaLonde, Yanzhong Pei, and Jeffrey Snyder, "Reevaluation of PbTe_{1-x} as high performance n-type thermoelectric material ," *Energy & Environmental Science* , vol. 4, p. 2090, 2011.
 - [55] Claude Barton, "Electron Effective Mass in PbS Single Crystals by Infrared Reflectivity Measurements ," *Journal of Applied Physics*, vol. 42, p. 445, 1971.