Thermodynamic Re-modeling of the Sb-Te System Using Associate and Ionic Models

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The Sb-Te system is re-modeled using the calculation of phase diagram (CALPHAD) technique. The liquid phase is modeled as (Sb, Sb_2Te_3, Te) using the associate model and as $(Sb^{3+})_p(Te^{2-},Te,Va)_q$ using the ionic model. The solution phases rhom(Sb) and hex(Te) are described as substitutional solutions. Two compounds, delta and gamma, are treated as $(Sb)_{0.4}(Sb,Te)_{0.6}$ according to their homogeneity ranges, while the compound Sb_2Te_3 follows a strict stoichiometry. A set of self-consistent thermodynamic parameters is obtained. Using these thermodynamic parameters, the experimental Sb-Te phase diagram, mixing enthalpies of liquid at 911 K and 935 K, activities of Sb and Te in liquid at 911 K and 1023 K, and Gibbs energy of liquid at 911 K, is well reproduced by the calculations. And the calculated enthalpy of formation, enthalpy of fusion, and heat capacity of Sb_2Te_3 are also in fairly good agreement with all the available experimental data.

Key words: Sb-Te system, thermoelectric materials, thermodynamic properties, CALPHAD technique

INTRODUCTION

In recent years, the investigation of Sb-Te alloys has received much attention due to their interesting properties. Sb_2Te_3, which is the most stable compound in the Sb-Te system and has a rhombohedral layered structure with space group $R\bar{3}m$, is the best thermoelectronic material in the temperature range of 200–400 K.[1,2] The phase change material used as a programming material for the phase change random access memory can be obtained when Ge and In elements are added to the Sb-Te system.[3,4] Additionally, Sb-Te alloys are still known as a topological insulator.[5–7]

Accurate phase diagram and thermochemical data can provide more reliable information for material preparation. Ghosh et al.[8] optimized the Sb-Te system using the ionic model for liquid according to the Gibbs energy data of pure elements Sb and Te in the Scientific Group Thermodata Europe (SGTE) substance database[9] and the

experimental data before 1989. Although the experimental activity of Sb in Ref. 10 was published after the work of Ghosh et al.,[8] this experimental measurement shows a good agreement with the theoretical calculation using the thermodynamic modeling by Ghosh et al.[8] (see fig. 5 in Ref. 10). However, the Gibbs energy functions for liquid(Sb), rhom(Sb), liquid(Te) and hex(Te) in the revised SGTE substance database[11] have been modified. Using the latest Gibbs energy functions of pure elements Sb and Te,[11] and the optimized parameters in Ref. 8, several inconsistencies between the tentative calculations and the results of Ref. 8 should be noted:

– The correct Sb-Te phase diagram cannot be obtained;
– For most of reaction temperatures of invariant reactions, there will exist a difference about 20 K from the results in Ref. 8;
– And the heat capacity of Sb_2Te_3 has a deviation from experimental data.[12–17]

On the basis of the phase diagram assessed by Ghosh[18] and the latest thermochemical data from Refs. 10, 16, 17, 19, 20, the Sb-Te system is optimized

using the associate and the ionic models in the present work.

LITERATURE INFORMATION

Phase Equilibria Data

The Sb-Te phase diagram was firstly determined by Fay and Ashley[21] using thermal analysis, in which the eutectic arrests on the cooling curves could not be detected and the continuous solid solubility was assumed between Sb and Sb_2Te_3. The shape of the liquidus curve was confirmed by Pélabon.[22] The thermoelectric and electrical conductivity data measured by Haken[23] and the magnetic susceptibility data by Honda and Soné[24] confirmed the fact of continuous solid solubility between Sb and Sb_2Te_3. Haken[23] and Veraksa et al.[25] determined the solid solubility of Te in rhom(Sb). The homogeneity range of Sb_2Te_3 has been investigated by many researchers.[26–31]

An eutectic reaction, liquid → rhom(Sb) + Sb_2Te_3, was indicated by thermal analysis and metallographic examinations.[32,33] However, Abrikosov et al.[34] thought this eutectic reaction occurred because the rapid cooling of melt prevented peritectic formation of the delta (δ) and gamma (γ) phases.

Abrikosov et al.[35] and Bordas[36] reinvestigated the phase equilibria by thermal analysis and x-ray diffraction (XRD). Two intermediate phases, δ and γ between Sb and Sb_2Te_3, were found and an azeotropic liquidus minimum was determined. Brown and Lewis[37] confirmed the azeotropic minimum, but reported only one intermediate phase with a composition range from 10 at.% to 60 at.% Te.

Eckerlin and Stegherr[38] measured the phase equilibria between Sb and Sb_2Te_3 using thermal analysis, metallography and XRD techniques. A peritectic reaction at 560°C was confirmed. They also reported the existence of 11 discrete phases in this composition range and did not observe the γ phase. The compounds with Sb concentration above 40 at.% were studied by many researchers,[39–46] showing that all the compounds are composed of bilayers of Sb and Sb_2Te_3.

Thermochemical Information

The enthalpies of mixing of liquid Sb-Te alloys at 911 K and 935 K were measured using calorimetry method by Feutelais et al.[19] and Maekawa et al.,[47] respectively. The activities of Sb and Te at 911 K and 1023 K were determined using the galvanic cells by Feutelais et al.[10] and Onderka and Fitzner,[20] respectively.

The enthalpy of formation,[12,48,49] enthalpy of fusion,[12,50] entropy of formation,[13,49] standard Gibbs energy of formation,[51] and heat capacity in different temperature ranges[12–17] for the compound Sb_2Te_3 were determined experimentally.

Ghosh[18] re-assessed the Sb-Te system according to the experimental data before 1992 and the calculated phase digram.[8] There are three solutions, liquid, rhom(Sb), and hex(Te), and three compounds, δ, γ, and Sb_2Te_3 in the Sb-Te system. The compounds δ and γ have the large homogeneity ranges of 16.4–36.8 at.% and 41.1–49.0 at.% Te, respectively.

THERMODYNAMIC MODEL

The Gibbs energy functions for the unary phases of elements Sb and Te are taken from the SGTE database of pure elements.[11]

In the Sb-Te system, many experimental results[31,52–61] have proved that there is a short range order around the composition of Sb_2Te_3 in liquid. In the present work, the ionic model $(Sb^{+3})_p$ $(Te^{-2}, Te, Va)_q$[62] and the associate model (Sb, Sb_2Te_3, Te) are used to describe this short range order in liquid, and the molar Gibbs energy is expressed as follows:

$$
\begin{aligned}
G^{liquid} =\; & x_{Sb}G_{Sb}^{liquid}(T) + x_{Te}G_{Te}^{liquid}(T) \\
& + x_{Sb_2Te_3}G_{Sb_2Te_3}^{liquid}(T) + RT(x_{Sb}\ln x_{Sb} \\
& + x_{Te}\ln x_{Te} + x_{Sb_2Te_3}\ln x_{Sb_2Te_3}) + {}^EG_m
\end{aligned}
\tag{1}
$$

$$
\begin{aligned}
G^{liquid} =\; & y_{Te^{-2}}\,G_{Sb^{+3}:Te^{-2}}^{liquid} + y_{Va}\,G_{Sb^{+3}:Va}^{liquid} + y_{Te}\,G_{Te}^{liquid} \\
& + qRT(y_{Te^{-2}}\ln y_{Te^{-2}} + y_{Va}\ln y_{Va} + y_{Te}\ln y_{Te}) \\
& + {}^EG_m
\end{aligned}
\tag{2}
$$

Equations 1 and 2 are the Gibbs energy functions of liquid using the associate model and the ionic model, respectively.

In Eq. 1, x_{Sb}, x_{Te} and $x_{Sb_2Te_3}$ are the mole fractions of the pure elements Sb, Te and the associate Sb_2Te_3, respectively. G_{Sb}^{liquid} and G_{Te}^{liquid} are the Gibbs energies of Sb and Te from SGTE pure elements database.[11] $G_{Sb_2Te_3}^{liquid}$ is the Gibbs energy of the associate Sb_2Te_3 in liquid.

In Eq. 2, $y_{Te^{-2}}$, y_{Te} and y_{Va} are the site fractions of Te^{-2}, Te and Va in the second sublattice, respectively.

${}^EG_m$ in both Eqs. 1 and 2 is the excess Gibbs energy of liquid and is expressed as Eqs. 3 and 4 for the associate model and the ionic model, respectively.

$$
\begin{aligned}
{}^EG_m =\; & x_{Sb}x_{Te}\sum_j {}^jL_{Sb,Te}(x_{Sb}-x_{Te})^j \\
& + x_{Sb}x_{Sb_2Te_3}\sum_j {}^jL_{Sb,Sb_2Te_3}(x_{Sb}-x_{Sb_2Te_3})^j \\
& + x_{Sb_2Te_3}x_{Te}\sum_j {}^jL_{Sb_2Te_3,Te}(x_{Sb_2Te_3}-x_{Te})^j
\end{aligned}
\tag{3}
$$

Table I. Thermodynamic parameters in the Sb-Te system

Phase	Thermodynamic parameters
liquid	Ionic model $(Sb^{+3})_p(Te^{-2},Te,Va)_q$

$$G_{Sb^{+3}:Te^{-2}}^{liq.} = 2G_{Sb}^{liq.} + 3G_{Te}^{liq.} - 102785.0 + 78.2515T$$

$${}^0L_{Sb^{+3}:Te^{-2},Te}^{liq.} = +51856.4 - 54.2642T$$

$${}^1L_{Sb^{+3}:Te^{-2},Te}^{liq.} = +13427.7 - 24.3722T$$

$${}^0L_{Sb^{+3}:Te^{-2},Va}^{liq.} = +25311.1 - 28.9116T$$

$${}^1L_{Sb^{+3}:Te^{-2},Va}^{liq.} = -24462.5 + 17.9377T$$

Associate model (Sb, Sb_2Te_3, Sb)

$${}^0G_{Sb_2Te_3}^{liq.} = 0.4G_{Sb}^{liq.} + 0.6G_{Te}^{liq.} - 20557.0 + 15.6503T$$

$${}^0L_{Sb_2Te_3,Te}^{liq.} = +8348.8 - 1.8429T$$

$${}^1L_{Sb_2Te_3,Te}^{liq.} = +1179.4 - 3.5931T$$

$${}^0L_{Sb_2Te_3,Sb}^{liq.} = +8559.3 - 3.6932T$$

$${}^1L_{Sb_2Te_3,Sb}^{liq.} = -4703.8 + 9.8773T$$

rhom(Sb)	Model (Sb,Te)

$${}^0G_{Te}^{rhom} = GHSER_{Te} + 5000.0$$

$${}^0G_{Sb,Te}^{rhom} = -4000.0$$

hex(Te)	Model (Sb,Te)

$${}^0G_{Sb}^{hex} = GHSER_{Sb} + 5000.0$$

Sb_2Te_3	Model $Sb_{0.4}Te_{0.6}$

$$0 < T \leq 60$$

$${}^0G_{Sb:Te}^{Sb_2Te_3} = -17961.5602 - 3.27284441T + 0.0294155953T^2$$
$$- 0.00185310048T^3 + 7.92008333 \times 10^{-6} \times T^4$$

$$60 \leq T < 1000$$

$${}^0G_{Sb:Te}^{Sb_2Te_3} = -19376.6 + 106.2655T - 22.5753T\ln(T) - 4.87264934 \times 10^{-3} \times T^2$$
$$+ 3.62456157 \times 10^{-7} \times T^3 + 12931.1094T^{-1}$$

gamma	Model $Sb_{0.4}(Sb,Te)_{0.6}$

$${}^0G_{Sb:Sb}^{gamma} = GHSER_{Sb} + 1460.0 - 0.4900T^{[a]}$$

$${}^0G_{Sb:Te}^{gamma} = {}^0G_{Sb:Te}^{Sb_2Te_3} + 872.2$$

$${}^0L_{Sb:Sb,Te}^{gamma} = -2835.6 + 9.3216T$$

$${}^1L_{Sb:Sb,Te}^{gamma} = +10593.5 - 10.1425T$$

delta	Model $Sb_{0.4}(Sb,Te)_{0.6}$

$${}^0G_{Sb:Sb}^{delta} = GHSER_{Sb} + 1070.0 - 0.3600T^{[a]}$$

$${}^0G_{Sb:Te}^{delta} = {}^0G_{Sb:Te}^{Sb_2Te_3} + 1471.4$$

$${}^0L_{Sb:Sb,Te}^{delta} = -6394.9 + 12.1759T$$

$${}^1L_{Sb:Sb,Te}^{delta} = +1425.0 + 0.9063T$$

$${}^2L_{Sb:Sb,Te}^{delta} = -2243.2$$

In J mol^{-1} of the formula units.[a]These data are taken from Ref. 8.

$$^{E}G_m = y_{Te^{-2}}y_{Te}\sum_j {}^{j}L_{Sb^{+3}:Te^{-2},Te}(y_{Te^{-2}} - y_{Te})^j$$

$$+ y_{Te^{-2}}y_{Va}\sum_j {}^{j}L_{Sb^{+3}:Te^{-2},Va}(y_{Te^{-2}} - y_{Va})^j \quad (4)$$

$$+ y_{Te}y_{Va}\sum_j {}^{j}L_{Sb^{+3}:Te,Va}(y_{Te} - y_{Va})^j$$

The solution phases, rhom(Sb) and hex(Te), are described using substitutional solution model, and the molar Gibbs energies are modeled as:

$$G_m^{\phi}(T) = x_{Sb}G_{Sb}^{\phi}(T) + x_{Te}G_{Te}^{\phi}(T)$$
$$+ RT(x_{Sb}\ln x_{Sb} + x_{Te}\ln x_{Te}) + {}^{E}G_m^{\phi} \quad (5)$$

where x_{Sb} and x_{Te} are the mole fractions of pure elements Sb and Te, respectively; ${}^{E}G_m^{\phi}$ is the excess Gibbs energy and is expressed by the Redlich–Kister polynomial,

$$^{E}G_m^{\phi} = x_{Sb}x_{Te}\sum_j {}^{j}L_{Sb,Te}^{\phi}(x_{Sb} - x_{Te})^j \quad (6)$$

where ^{j}L in Eqs. 3, 4 and 6 is the interaction parameter for liquid, rhom(Sb), and hex(Te), and is expressed as the following equation:

$$^{j}L = a_j + b_jT \quad (7)$$

where a_j and b_j are the parameters to be optimized in the present work.

Among three intermetallic compounds, δ, γ, and Sb_2Te_3, Sb_2Te_3 has a small homogeneity range from 59 at.% to 59.6 at.% Te[27–31] and is treated as a stoichiometric compound in the present work. The molar Gibbs energy is expressed as:

$$G^{Sb_2Te_3} = a + bT + cT\ln(T) + dT^2 + eT^3 + fT^{-1} \quad (8)$$

where a, b, c, d, e, and f are the parameters to be optimized according to the thermochemical experimental data, such as the heat capacity, enthalpy of formation, and enthalpy of fusion of Sb_2Te_3.

Table II. Invariant reactions of the Sb-Te system

Reaction	T (K)	x(Sb)			Refs.
liq. + rhom(Sb) → delta	823	0.25	0.01	0.18	35
	823	0.247	0.025	0.169	36
	821	0.231	0.013	0.164	8
	823	0.2556	0.0281	0.1605	Ionic model
	822	0.2443	0.0279	0.1605	Associate model
liq. → delta	811	0.32	0.32		35
	817	0.31	0.31		36
	818	0.277	0.277		8
	818	0.3052	0.3052		Ionic model
	818	0.2927	0.2927		Associate model
liq. + gamma → delta	821	0.37	0.42	0.39	35
	821	0.350	0.406	0.370	36
	819	0.308	0.411	0.368	8
	820	0.3514	0.4257	0.3949	Ionic model
	821	0.3447	0.4257	0.3950	Associate model
liq. + Sb_2Te_3 → gamma	831	0.41	0.6	0.55	35
	831	0.381	0.59	0.539	36
	830	0.367	0.596	0.490	8
	832	0.4123	0.6	0.4859	Ionic model
	833	0.4064	0.6	0.4859	Associate model
liq. → Sb_2Te_3	889				31, 35, 36
	892				12
	894				50
	891				8
	890				Ionic model
	894				Associate model
liq. → Sb_2Te_3 + hex(Te)	693	0.91	0.6	1.0	35
	697	0.89	0.6	1.0	37
	715	0.9	0.6	1.0	32, 33
	719	0.9	0.6	1.0	21
	725	0.9	0.6	1.0	22
	695	0.926	0.600	1.0	8
	695	0.9208	0.6	1.0	Ionic model
	688	0.9262	0.6	1.0	Associate model

The compounds δ and γ have large homogeneity ranges and are treated as $Sb_{0.4}(Sb,Te)_{0.6}$ according to Ref. 8. And the Gibbs energy expression of δ or γ is as the following:

$$G_m^\phi = y_{Sb} G_{Sb:Sb}^\phi + y_{Te} G_{Sb:Te}^\phi + 0.6RT(y_{Sb} \ln y_{Sb} + y_{Te} \ln y_{Te}) + y_{Sb}y_{Te} \sum_j {}^j L_{Sb,Te}^\phi (y_{Sb} - y_{Te})^j \tag{9}$$

where $G_{Sb:Sb}^\phi$ and $G_{Sb:Te}^\phi$ ($\phi = \delta$ or γ) represent the Gibbs energies of Sb and Sb_2Te_3 with the crystal structure of the phase ϕ. y_{Sb} and y_{Te} are the site fractions of Sb and Te in the second sublattice, respectively.

ASSESSMENT PROCEDURE

The optimization was carried out by means of the optimization module PARROT of the thermodynamic software Thermo-Calc,[63] which can handle various kinds of experimental data. In the beginning of optimization, the coefficients c, d, e, and f in Eq. 8 of the molar Gibbs energy expression of Sb_2Te_3, are optimized according to the heat capacities reported by Refs. 12–17. Then, a and b in Eq.8 and the thermodynamic parameters of liquid are optimized according to the mixing enthalpy, activity, Gibbs energy, and entropy of liquid, as well as the liquidus and melting point of Sb_2Te_3. In order to avoid the unlimited negative value of the heat capacity of Sb_2Te_3 at $T \to 0$ K, the heat capacity function of Sb_2Te_3 is divided into two parts, $0 < T \leq 60$ K and $T \geq 60$ K. The heat capacity above 60 K is optimized based on the experimental data[12–17] and that below 60 K is derived from the optimized Gibbs energy above 60 K. In order to obtain a continuous segmented function, the enthalpy, entropy, heat capacity, and the first and second derivatives of heat capacity, which are calculated from the optimized Gibbs energy below and above 60 K, are kept to be equal at the intersection point.

RESULTS AND DISCUSSIONS

The thermodynamic parameters of the Sb-Te system obtained in the present work are shown in Table I. The liquid phase can be described using either the ionic model or the associate model. The calculated invariant equilibria in the Sb-Te system and the experimental data are listed in Table II. A satisfactory agreement is obtained between the experiments and the calculated results.

Figure 1a is the calculated Sb-Te phase diagram using the associate and the ionic models for liquid in comparison with the experimental data.[21,22,31–33,35,36] Both models can well reproduce the phase diagram with very small differences. Figure 1b is the calculated Sb-Te phase diagram without experimental data which aims to present the calculated results more clearly.
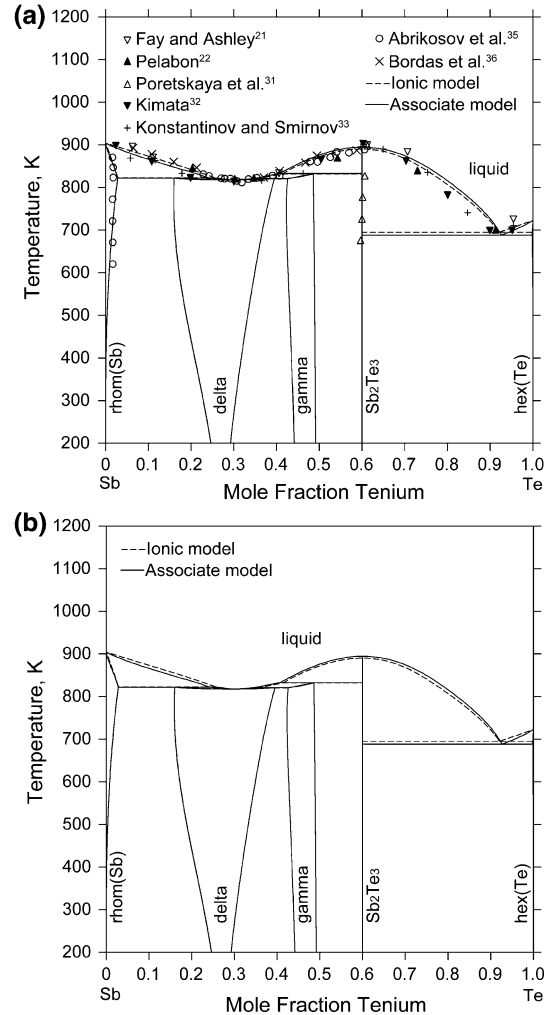

Fig. 1. (a) Calculated Sb-Te phase diagram using associate and ionic models for liquid in comparison with experimental data.[21,22,31–33,35,36] (b) Calculated Sb-Te phase diagram using associate and ionic models for liquid.
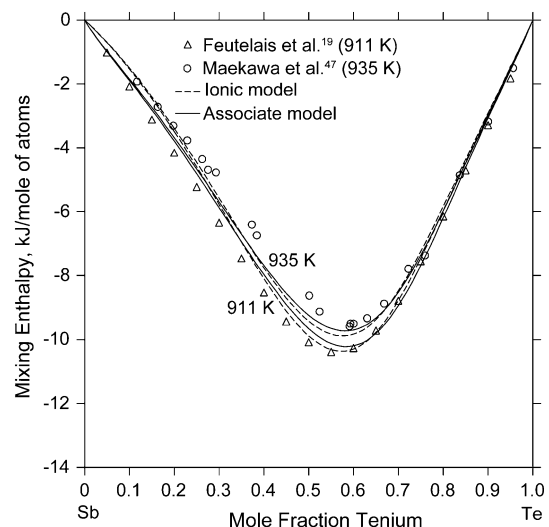

Fig. 2. Calculated mixing enthalpy of liquid at 911 K and 935 K in comparison with experimental data.[19,46]

The calculated mixing enthalpies of liquid at 911 K and 935 K, mixing Gibbs energy of liquid at 911 K, partial molar Gibbs energies of Sb and Te in liquid at 911 K, and activities of Sb and Te in liquid at 911 and 1023 K are presented in Figs. 2, 3, 4, and 5, respectively. In Figs. 2, 3, 4, and 5, the solid lines and the dashed lines are respectively calculated using the associate model and the ionic model with the liquid phase as the reference states for both Sb and Te. As shown in Figs. 2, 3, 4, and 5, the present calculated and the literature reported thermochemical data are consistent with each other.

Figure 6 gives the calculated enthalpy of Sb_2Te_3 in comparison with the experimental data.[15,17] The calculated enthalpy of formation at 298 K, and enthalpy and entropy of fusion at the melting point of Sb_2Te_3 are listed in Table III. As shown in Fig. 6
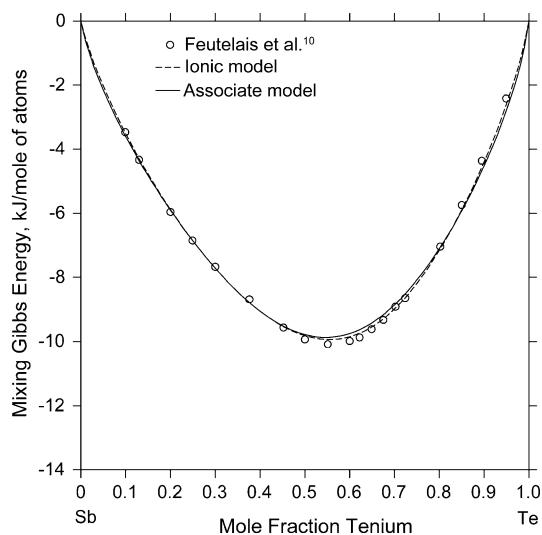

Fig. 3. Calculated mixing Gibbs energy of liquid at 911 K in comparison with experimental data.[10]
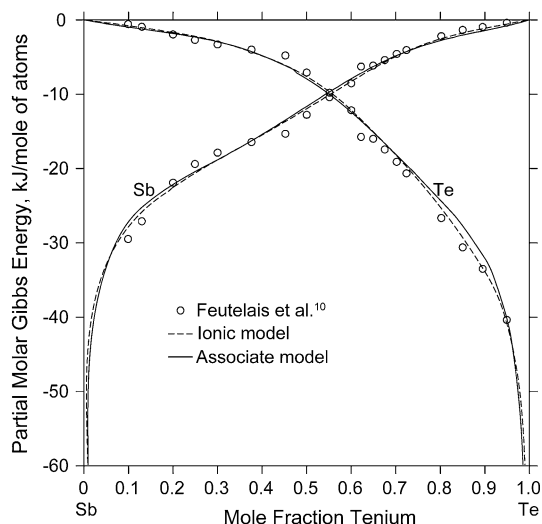

Fig. 4. Calculated partial molar Gibbs energy of Sb and Te in liquid at 911 K in comparison with experimental data.[10]
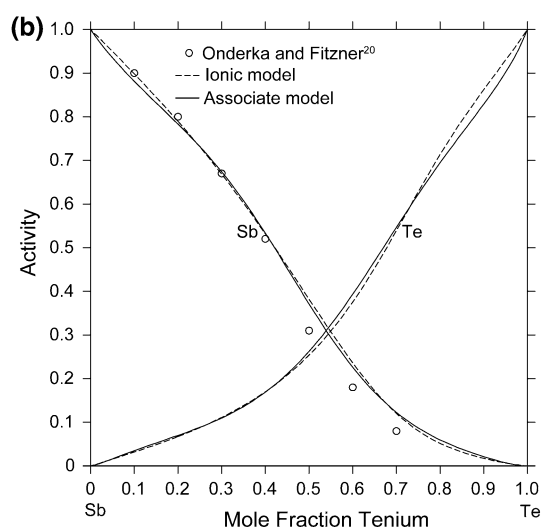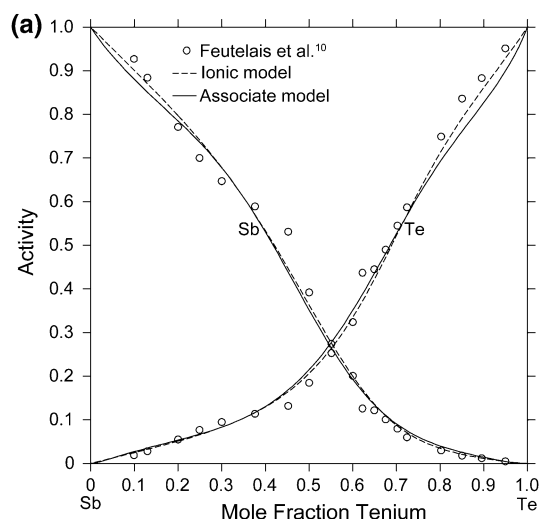

Fig. 5. (a) Calculated activity of Sb and Te in liquid at 911 K in comparison with experimental data.[10] (b) Calculated activity of Sb and Te in at 1023 K in comparison with experimental data.[20]
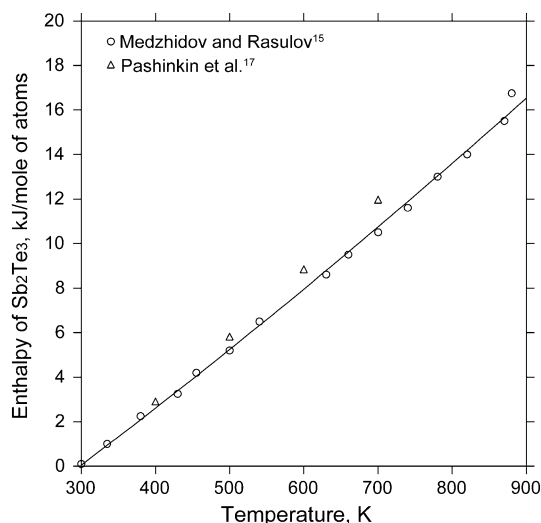

Fig. 6. Calculated enthalpy of Sb_2Te_3 in comparison with the experimental data.[15,17]

Table III. Enthalpy of formation and fusion and entropy of fusion of Sb$_2$Te$_3$

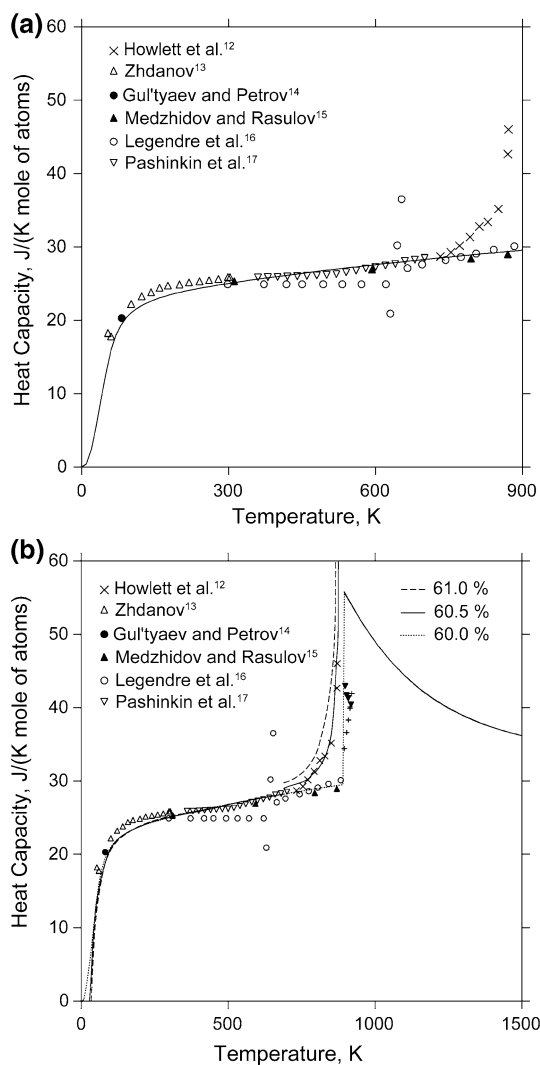|	Associate model	Ionic model	Ref. 12	Ref. 48	Ref. 49	Ref. 50
Enthalpy of formation (kJ/mole of atoms)	−12.145	−12.145	−11.30	−14.90	−12.33	
Enthalpy of fusion (kJ/mole of atoms)	20.893	20.715	19.79			20.00
Entropy of fusion (J/mole of atoms K)	23.37	23.48	22.5			

(a)

(b)

Fig. 7. (a) Calculated heat capacity of Sb$_2$Te$_3$ in comparison with the experimental data.[12–17] (b) Calculated heat capacity of the Sb-Te system at 60.0 at.%, 60.5 at.%, and 61.0 at.% Te in comparison with the experimental data[12–17] at 60.0 at.% Te using associate model for liquid.

Fig. 8. Calculated mole fraction of species in liquid at 935 K.

and Table III, a very good consistence is obtained between the calculated results and the experimental data.

The calculated heat capacity of Sb$_2$Te$_3$ is presented in Fig. 7, in which the experimental heat capacity below 700 K is reproduced well. However, the calculated value has a big deviation from the experimental data measured by Howlett et al.,[12]
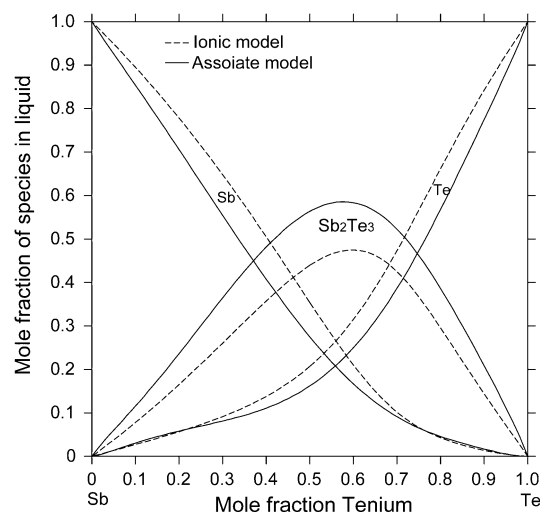
who stated that the accelerated increase in the heat capacity of Sb$_2$Te$_3$ could have been caused by the presence of impurities or by segregation in samples. The heat capacities of the Sb-Te alloys at 60.0 at.%, 60.5 at.%, and 61.0 at.% Te are calculated and shown in Fig. 7b, for which the thermodynamic parameters of liquid from the associate model are used. The calculated results at 60.5 at.% Te can well reproduce the experimental data[12] including those in the temperature range of 700–900 K. Maybe it is the volatility of Sb in the specimens which means the composition of alloys[12] is located in the liquid + Sb$_2$Te$_3$ phase region. However, the experimental heat capacity data of liquid[12,16] were not reproduced well, as shown in Fig. 7b. During the process of optimization, the experimental results including the liquidus of Sb$_2$Te$_3$ in the Te-rich side,[22,32,33] the mixing enthalpies of liquid at 911 K and 935 K,[19,47] the mixing Gibbs energy of liquid at 911 K[10] and the activities of Sb and Te in liquid at 911 K[10] will not be reproduced if the experimental heat capacity data of liquid[12,16] were fitted well.

Figure 8 is the calculated mole fraction of species in liquid at 935 K, and it presents the short range order in liquid.

CONCLUSIONS

The phase relationships and thermodynamic properties in the Sb-Te system are critically optimized on the basis of the experimental information

available in the literature. A set of self-consistent thermodynamic parameters describing the Gibbs energies of individual phases in the Sb-Te system as the functions of composition and temperature is obtained. With the present optimized parameters, one can make various thermodynamic calculations of practical interest.

ACKNOWLEDGEMENTS

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