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Thermodynamic Modeling of the Pt-Te and Pt-Sb-Te Systems

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The Pt-Te and the Pt-Sb-Te systems are modeled using the calculation of phase diagram (CALPHAD) technique. In the Pt-Te system, the liquid phase is modeled as (Pt, PtTe$_2$, Te) using the associate model, and four intermediates, PtTe$_2$, Pt$_2$Te$_3$, Pt$_3$Te$_4$ and PtTe, are treated as stoichiometric compounds and their enthalpies of formation are obtained by means of first-principles calculations. The solution phases, fcc(Pt) and hex(Te), are described as substitutional solutions. Combined with the thermodynamic models of the liquid phase in the Pt-Sb and Sb-Te systems in the literature, the liquid phase of the Pt-Sb-Te ternary system is modeled as (Pt, Sb, Te, Sb$_2$Te$_3$, PtTe$_2$) also using the associate model. The compounds, PtTe$_2$, Pt$_2$Te$_3$, Pt$_3$Te$_4$ and PtTe in the Pt-Te system and PtSb$_2$, PtSb, Pt$_3$Sb$_2$ and Pt$_7$Sb in the Pt-Sb system are treated as line compounds Pt$_m$(Sb,Te)$_n$ in the Pt-Sb-Te system, and the compound Pt$_5$Sb is treated as (Pt,Sb)$_5$(Pt,Sb,Te). A set of self-consistent thermodynamic parameters is obtained. Using these thermodynamic parameters, the experimental Pt-Te phase diagram, the experimental heat capacities of PtTe and PtTe$_2$, the enthalpies of formation from first-principles calculations for PtTe$_2$, Pt$_2$Te$_3$, Pt$_3$Te$_4$, and PtTe, and the ternary isothermal sections at 873 K, 923 K, 1073 K and 1273 K are well reproduced.

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

INTRODUCTION

Platinum can be used as the plating of electrodeposition of Sb$_2$Te$_3$ thermoelectric materials, so the interfacial phase equilibria among Pt, Sb and Te are very important to obtain thin film thermoelectric alloys.[1] Additionally, the platinum group elements commonly form compounds with S, Sb, Te, As, Se, Bi, Sn, Fe, Sb, Hg, Ni, Cu, etc., so most of the platinum group minerals exhibit complex compositions.[2] Because of the existence of platinum antimonides and tellurides in nature, the phase relationships in the Pt-Sb-Te system are very important for mineralogists.[3]

In this study, the phase diagram of the Pt-Te binary system and the isothermal sections of the Pt-Sb-Te ternary system at 873, 923, 1073 and

1273 K are critically evaluated and the thermodynamic parameters for each phase of the systems are optimized in order to obtain complete phase equilibria information.

LITERATURE INFORMATION

Pt-Te System

The partial phase diagram between Pt and PtTe$_2$ was first determined by Gimpl et al.[4] Two intermediate compounds, PtTe and PtTe$_2$, were reported. But the liquidus between PtTe$_2$ and hex(Te) was not mentioned. Bhan et al.[5] measured the Pt-Te phase diagram, and four compounds, PtTe, PtTe$_2$, Pt$_3$Te$_4$ and Pt$_2$Te$_3$, were determined. However, the liquidus between PtTe$_2$ and hex(Te) was still shown as a dashed line.

In order to confirm the existence of the above compounds and liquidus between PtTe$_2$ and Te, Kim[6]

re-investigated the Pt-Te system by reflected light microscopy, x-ray diffraction (XRD), and electron probe microanalysis (EPMA). Four compounds, PtTe, Pt_3Te_4, Pt_2Te_3 and $PtTe_2$, were confirmed, and the solid solubilities of Te in fcc(Pt) and Pt in hex(Te) were less than 0.5 at.%. Two eutectic reactions, liquid → PtTe + fcc(Pt) at 1143 K and liquid → $PtTe_2$ + hex(Te) at 722 K, and two peritectic reactions, liquid + $PtTe_2$ → Pt_3Te_4 at > 1273 K and liquid +Pt_3Te_4 → PtTe at 1208 K, and one peritectoid reaction, Pt_3Te_4 + $PtTe_2$ → Pt_2Te_3 between 923 K and 973 K, were recommended.

The enthalpies of formation of PtTe and Pt Te_2 were given by Karzhavin[7] by means of the comparative methods. Grønvold et al.[8] and Westrum et al.[9] determined the heat capacities of PtTe and $PtTe_2$ by means of calorimeter.

Sb-Te System

The Sb-Te system was optimized by Ghosh et al.[10] using the ionic model for liquid and by Guo et al.[11] using both the ionic model and the associate model for liquid. The thermodynamic parameters obtained by Guo et al.[11] were used in the present work because the latest pure element Gibbs energies of Sb and Te were used. Figure 1 presents the calculated Sb-Te phase diagram using the thermodynamic parameters of Ref. 11, in which liquid was described using the associate model (Sb, Sb_2Te_3, Te).

Pt-Sb System

The Pt-Sb system was optimized by Liu et al.[12] and Guo et al.[13] In order to keep the thermodynamic parameters consistent, the optimized thermodynamic parameters of Ref. 13 were adopted in the present work. Figure 2 shows the calculated Pt-Sb phase diagram.

Pt-Sb-Te System

The isothermal section of the Pt-Sb-Te system at 923 K was first determined by El-Boragy and Schubert,[14] and no ternary compound was found.

The phase relationships at 873 K, 1073 K and 1273 K were studied by Kim and Chao in 1990.[15] Later on, the isothermal sections at 873 K, 1073 K and 1273 K were reported by Kim,[3,16,17] respectively, which were almost the same as the results of Ref. 15.

THERMODYNAMIC MODEL

The Gibbs energy functions for the unary phases of elements Pt, Sb and Te are taken from the Scientific Group Thermodata Europe (SGTE) database of pure elements.[18]

Pt-Te System

In the Pt-Te system, the liquidus in the left and right sides of the compound $PtTe_2$ is very asymmetric, and it is hard to obtain such asymmetric liquidus using the substitution model (Pt, Te) for liquid. Since Te and Pt are always anion and cation, respectively, in the compounds, the ionic model for liquid is appropriate in the Pt-Te system. However, Pt can form Pt^{+2}, Pt^{+4}, or Pt^{+6}, which will make the ionic model complicated. In the present work, the associate model (Pt, $PtTe_2$, Te) is used to describe the liquid instead of the ionic model. The molar Gibbs energy is expressed as follows:
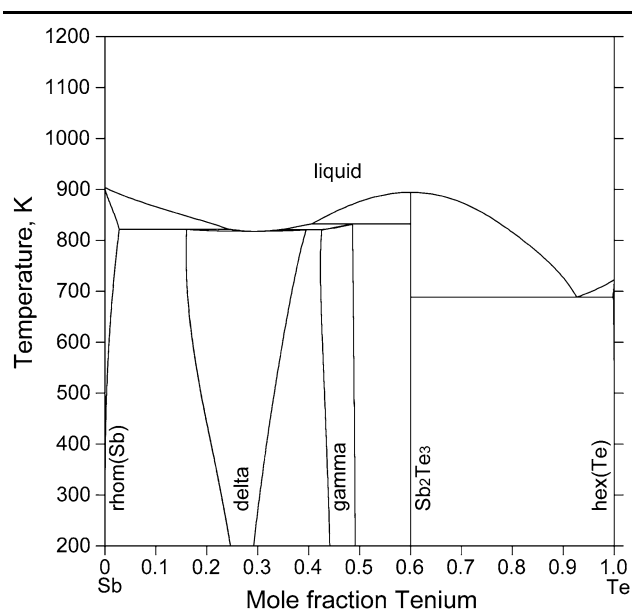

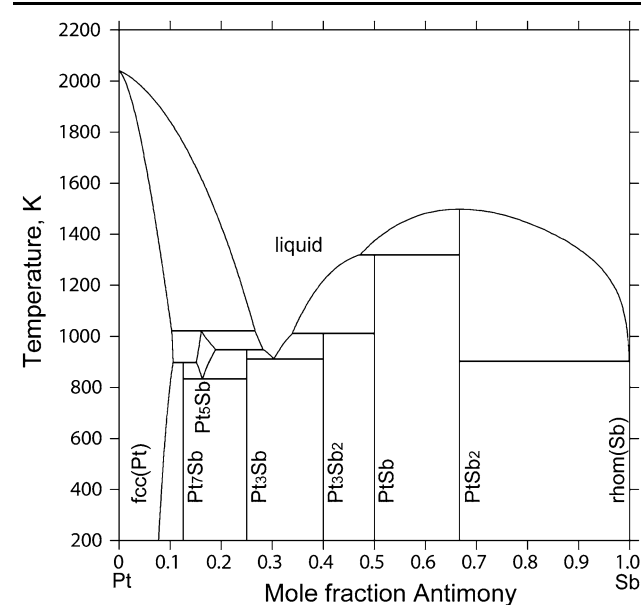Fig. 1. Calculated Sb-Te phase diagram using the thermodynamic parameters in Ref. 11.

Fig. 2. Calculated Pt-Sb phase diagram using the thermodynamic parameters in Ref. 13.

$$G^{\text{liquid}} = x_{\text{Pt}} G_{\text{Pt}}^{\text{liquid}}(T) + x_{\text{Te}} G_{\text{Te}}^{\text{liquid}}(T) + x_{\text{PtTe}_2} G_{\text{PtTe}_2}^{\text{liquid}}(T)$$
$$+ RT(x_{\text{Pt}} \ln x_{\text{Pt}} + x_{\text{Te}} \ln x_{\text{Te}}$$
$$+ x_{\text{PtTe}_2} \ln x_{\text{PtTe}_2}) + {}^E G_m,$$
$$(1)$$

where x_{Pt}, x_{Te} and x_{PtTe_2} are the mole fractions of the pure elements Pt, Te and the associate PtTe_2, respectively. $G_{\text{Pt}}^{\text{liquid}}$ and $G_{\text{Te}}^{\text{liquid}}$ are the Gibbs energies of Pt and Te from the SGTE pure elements database[18] and $G_{\text{PtTe}_2}^{\text{liquid}}$ is the Gibbs energy of the associate PtTe_2 in liquid. ${}^E G_m$ is the excess Gibbs energy of liquid and is expressed as Eq. 2.

$${}^E G_m = x_{\text{Pt}} x_{\text{Te}} \sum_j {}^j L_{\text{Pt},\text{Te}} (x_{\text{Pt}} - x_{\text{Te}})^j$$
$$+ x_{\text{Pt}} x_{\text{PtTe}_2} \sum_j {}^j L_{\text{Pt},\text{PtTe}_2} (x_{\text{Pt}} - x_{\text{PtTe}_2})^j \quad (2)$$
$$+ x_{\text{PtTe}_2} x_{\text{Te}} \sum_j {}^j L_{\text{PtTe}_2,\text{Te}} (x_{\text{PtTe}_2} - x_{\text{Te}})^j.$$

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

$$G_m^\phi(T) = x_{\text{Pt}} G_{\text{Pt}}^\phi(T) + x_{\text{Te}} G_{\text{Te}}^\phi(T)$$
$$+ RT(x_{\text{Pt}} \ln x_{\text{Pt}} + x_{\text{Te}} \ln x_{\text{Te}}) + {}^E G_m^\phi, \quad (3)$$

where ${}^E G_m^\phi$ is the excess Gibbs energy and is expressed by the Redlich–Kister polynomial,

$${}^E G_m^\phi = x_{\text{Pt}} x_{\text{Te}} \sum_j {}^j L_{\text{Pt},\text{Te}}^\phi (x_{\text{Pt}} - x_{\text{Te}})^j. \quad (4)$$

${}^j L$ in Eqs. 2 and 4 is the interaction parameter for liquid, fcc(Pt) and hex(Te), and is expressed as the following equation:

$${}^j L = a_j + b_j T, \quad (5)$$

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

The intermetallic compounds Pt_3Te_4 and Pt_2Te_3 in the Pt-Te system are treated as stoichiometric

compounds in the present work. Due to a lack of experimental heat capacity data, the molar Gibbs energy of Pt_mTe_n is expressed as:

$$G^{\text{Pt}_m\text{Te}_n} = m\text{GHSER}_{\text{Pt}} + n\text{GHSER}_{\text{Te}} + \Delta G_f^{\text{Pt}_m\text{Te}_n}, \quad (6)$$

where $\Delta G_f^{\text{Pt}_m\text{Te}_n}$ is the Gibbs energy of formation of compounds and is expressed as following:

$$\Delta G_f^{\text{Pt}_m\text{Te}_n} = a + bT, \quad (7)$$

where a and b are the parameters to be optimized according to the enthalpy of formation obtained from first-principles calculations in the present work and the experimental phase relationships in Refs. 4–6.

For the intermetallic compounds PtTe and PtTe_2, the heat capacity data are available from literature.[7–9] These two compounds are also treated as stoichiometric compounds in the present work, while each of the Gibbs energy functions is described as a two-piecewise polynomial with the high and the low temperature parts according to the experimental heat capacity data.

Taking PtTe as an example, the Gibbs energy function is divided into two parts. Considering the experimental heat capacity data of Grønvold et al.,[8] the Gibbs energy functions are expressed as follows:

$$0 < T < 80 \text{ K}$$
$$G_{m1}^{\text{PtTe}} = a + bT + cT^3 + dT^4, \quad (8)$$

$$T \geq 80 \text{ K}$$
$$G_{m2}^{\text{PtTe}} = e + fT + gT\ln(T) + hT^2 + mT^{-1} + nT^3, \quad (9)$$

where a, b, c, d, e, f, g, h, m and n are the parameters to be optimized according to the experimental heat capacity and phase relationships. During the process of optimization, the following conditions between the high and the low temperature parts, $G_{m1}^{\text{PtTe}} = G_{m2}^{\text{PtTe}}$, $H_{m1}^{\text{PtTe}} = H_{m2}^{\text{PtTe}}$, $S_{m1}^{\text{PtTe}} = S_{m2}^{\text{PtTe}}$, $Cp_{m1}^{\text{PtTe}} = Cp_{m2}^{\text{PtTe}}$ and $\frac{dCp_{m1}}{dT} = \frac{dCp_{m2}}{dT}$, should be met when T equals 80 K.

Table I. Space groups (*SG*), atoms per primitive cell, and *k*-point meshes used for first-principles calculations of Pt, Te, PtTe, Pt$_3$Te$_4$, Pt$_2$Te$_3$, and PtTe$_2$ along with the calculated equilibrium volumes (Å^3/atom) at 0 K using PBE exchange–correlation functionals and experimental data

Material	SG	Atoms	*k*-mesh	E_0 (ev/cell)	PBE	Experimental volume (Å^3/atom)
Pt	$Fm\bar{3}m$	4	$16 \times 16 \times 16$	-24.412	15.5927	15.09[21]
Te	P3$_1$21	3	$16 \times 16 \times 16$	-9.426	34.8087	33.6897[22]
PtTe	$C2/m$	8	$10 \times 16 \times 10$	-39.715	23.8074	22.3875[3]
Pt$_3$Te$_4$	$C2/m$	14	$10 \times 16 \times 6$	-67.028	24.5621	23.2929[16]
Pt$_2$Te$_3$	$C2/m$	20	$9 \times 15 \times 4$	-94.173	25.0268	23.345[16]
PtTe$_2$	$P\bar{3}m1$	3	$19 \times 19 \times 12$	-13.572	25.8098	23.6667[23]

Table II. Thermodynamic parameters in the Pt-Sb-Te system[a]

Phase	Thermodynamic parameters	Ref.
liquid	Model $(Pt, Sb, Te, Sb_2Te_3, PtTe_2)_1$	
	$^0L_{Pt,Sb}^{liquid} = -169878.6 + 44.8959T$	13
	$^1L_{Pt,Sb}^{liquid} = -50982.5 + 9.1148T$	13
	$G_{Sb_2Te_3}^{liquid} = 0.4GLIQ_{Sb} + 0.6GLIQ_{Te} - 20557.0 + 15.6503T$	11
	$^0L_{Sb_2Te_3,Te}^{liquid} = +8348.8 - 1.8429T$	11
	$^1L_{Sb_2Te_3,Te}^{liquid} = +1179.4 - 3.5931T$	11
	$^0L_{Sb,Sb_2Te_3}^{liquid} = +8559.3 - 3.6932T$	11
	$^1L_{Sb,Sb_2Te_3}^{liquid} = -4703.8 + 9.8773T$	11
	$G_{PtTe_2}^{liquid} = 0.333GLIQ_{Pt} + 0.667GLIQ_{Te} - 31029.9 + 4.6984T$	This work
	$^0L_{Pt,PtTe_2}^{liquid} = -26718.2 + 12.0857T$	This work
	$^1L_{Pt,PtTe_2}^{liquid} = +7740.0$	This work
	$^0L_{PtTe_2,Te}^{liquid} = +18086.5 - 2.3028T$	This work
	$^1L_{PtTe_2,Te}^{liquid} = +4165.6$	This work
	$^0L_{Pt,PtTe_2,Sb}^{liquid} = -50000.0$	This work
	$^0L_{PtTe_2,Sb_2Te_3}^{liquid} = +20000.0$	This work
hex(Te)	Model $(Pt, Sb, Te)_1$	
	G(hex,Pt;0) = GHSER$_{Pt}$ + 5000.0	This work
	G(hex,Sb;0) = GHSER$_{Sb}$ + 5000.0	This work
fcc(Pt)	Model $(Pt, Sb, Te)_1(Va)_1$	
	G(fcc, Te;0) = GHSER$_{Te}$ + 5000.0	
	$^0L_{Pt,Sb}^{fcc} = -13004.2 + 60.7336T$	13
	$^1L_{Pt,Sb}^{fcc} = -222530.2$	13
	$^0L_{Pt,Te}^{fcc} = +35966.7$	This work
	$^1L_{Pt,Te}^{fcc} = +52726.7$	This work
rhom(Sb)	Model $(Pt, Sb, Te)_1$	
	G(rhom,Pt;0) = GHSER$_{Pt}$ + 5000.0	13
	G(rhom,Te;0) = GHSER$_{Te}$ + 5000.0	11
	$^0L_{Sb,Te}^{rhom} = -4000.0$	11
Pt$_7$Sb	Model Pt$_7$(Sb,Te)	
	$G_{Pt:Sb}^{Pt_7Sb} = 7GHSER_{Pt} + GHSER_{Sb} - 150253.0 + 26.8127T$	13
	$G_{Pt:Te}^{Pt_7Sb} = G_{Pt:Te}^{PtTe} + 7GHSER_{Pt} + 40000.0$	This work
Pt$_5$Sb	Model $(Pt,Sb)_5$ (Pt,Sb,Te)	
	$G_{Pt:Sb}^{Pt_5Sb} = 5GHSER_{Pt} + GHSER_{Sb} - 126606.3 + 28.7544T$	13
	$G_{Pt:Pt}^{Pt_5Sb} = 6GHSER_{Pt} + 30000.0$	13
	$G_{Sb:Sb}^{Pt_5Sb} = 6GHSER_{Sb} + 30000.0$	13
	$G_{Sb:Pt}^{Pt_5Sb} = G_{Pt:Pt}^{Pt_5Sb} + G_{Sb:Sb}^{Pt_5Sb} - G_{Pt:Sb}^{Pt_5Sb}$	13
	$^0L_{Pt,Sb:Pt}^{Pt_5Sb} = ^0L_{Pt,Sb:Sb}^{Pt_5Sb} = -558341.2$	13
	$^1L_{Pt,Sb:Pt}^{Pt_5Sb} = ^1L_{Pt,Sb:Pt}^{Pt_5Sb} = +190567.2$	13
	$^0L_{Pt:Pt,Sb}^{Pt_5Sb} = ^0L_{Sb:Pt,Sb}^{Pt_5Sb} = -111626.8$	13
	$G_{Pt:Te}^{Pt_5Sb} = G_{Pt:Te}^{PtTe} + 4GHSER_{Pt} + 30000.0$	This work
	$G_{Sb:Te}^{Pt_5Sb} = 1.667G_{Sb:Te}^{Sb_2Te_3} + 4.333GHSER_{Sb} + 30000.0$	This work

Table II. continued

Phase	Thermodynamic parameters	Ref.
Pt$_3$Sb	Model Pt$_3$(Sb,Te)	
	$G_{\mathrm{Pt:Sb}}^{\mathrm{Pt_3Sb}} = 3\mathrm{GHSER}_{\mathrm{Pt}} + \mathrm{GHSER}_{\mathrm{Sb}} - 104971.6 + 8.4047T$	13
	$G_{\mathrm{Pt:Te}}^{\mathrm{Pt_3Sb}} = G_{\mathrm{Pt:Te}}^{\mathrm{PtTe}} + 2\mathrm{GHSER}_{\mathrm{Pt}} + 20000.0$	This work
Pt$_3$Sb$_2$	Model Pt$_3$(Sb,Te)$_2$	
	$G_{\mathrm{Pt:Sb}}^{\mathrm{Pt_3Sb_2}} = 3\mathrm{GHSER}_{\mathrm{Pt}} + 2\mathrm{GHSER}_{\mathrm{Sb}} - 174658.4 + 10.8848T$	13
	$G_{\mathrm{Pt:Te}}^{\mathrm{Pt_3Sb_2}} = 2G_{\mathrm{Pt:Te}}^{\mathrm{PtTe}} + \mathrm{GHSER}_{\mathrm{Pt}} + 25000.0$	This work
	$^0L_{\mathrm{Pt:Sb,Te}}^{\mathrm{Pt_3Sb_2}} = -11552.7$	This work
PtSb	Model Pt(Sb,Te)	
	$G_{\mathrm{Pt:Sb}}^{\mathrm{PtSb}} = \mathrm{GHSER}_{\mathrm{Pt}} + \mathrm{GHSER}_{\mathrm{Sb}} - 81220.5 + 6.8230T$	13
	$G_{\mathrm{Pt:Te}}^{\mathrm{PtSb}} = G_{\mathrm{Pt:Te}}^{\mathrm{PtTe}} + 10000.0$	This work
	$^0L_{\mathrm{Pt:Sb,Te}}^{\mathrm{PtSb}} = +33456.1 - 36.1949T$	This work
PtSb$_2$	Model Pt(Sb,Te)$_2$	
	$G_{\mathrm{Pt:Sb}}^{\mathrm{PtSb_2}} = \mathrm{GHSER}_{\mathrm{Pt}} + 2\mathrm{GHSER}_{\mathrm{Sb}} - 149612.0 - 21.4560T$ $+7.078251T\ln(T)$	This work
	$G_{\mathrm{Pt:Te}}^{\mathrm{PtSb_2}} = G_{\mathrm{Pt:Te_2}}^{\mathrm{PtTe_2}} + 15000.0$	This work
	$^0L_{\mathrm{Pt:Sb,Te}}^{\mathrm{PtSb_2}} = +575.1 + 0.6441T$	This work
	$^1L_{\mathrm{Pt:Sb,Te}}^{\mathrm{PtSb_2}} = -19263.8$	
Sb$_2$Te$_3$	Model Sb$_{0.4}$Te$_{0.6}$	
	$0 < T < 60$	
	$^0G_{\mathrm{Sb:Te}}^{\mathrm{Sb_2Te_3}} = -17961.5602 - 3.27284441T + 0.0294155953T^2$ $-0.00185310048T^3 + 7.92008333 \times 10^{-6}T^4$	11
	$60 < T < 1000$	
	$^0G_{\mathrm{Sb:Te}}^{\mathrm{Sb_2Te_3}} = -19376.6 + 106.2655T - 22.5753T\ln(T) - 4.87264934$ $\times 10^{-3}T^2 + 3.62456157 \times 10^{-7}T^3 + 12931.1094T^{-1}$	11
gamma	Model Sb$_{0.4}$(Sb,Te)$_{0.6}$	
	$^0G_{\mathrm{Sb:Sb}}^{\mathrm{gamma}} = \mathrm{GHSER}_{\mathrm{Sb}} + 1460.0 - 0.4900T$	11
	$^0G_{\mathrm{Sb:Te}}^{\mathrm{gamma}} = {}^0G_{\mathrm{Sb:Te}}^{\mathrm{Sb_2Te_3}} + 872.2$	11
	$^0L_{\mathrm{Sb:Sb,Te}}^{\mathrm{gamma}} = -2835.6 + 9.3216T$	11
	$^1L_{\mathrm{Sb:Sb,Te}}^{\mathrm{gamma}} = +10593.5 - 10.1425T$	11
delta	Model Sb$_{0.4}$(Sb,Te)$_{0.6}$	
	$^0G_{\mathrm{Sb:Sb}}^{\mathrm{delta}} = \mathrm{GHSER}_{\mathrm{Sb}} + 1070.0 - 0.3600T$	11
	$^0G_{\mathrm{Sb:Te}}^{\mathrm{delta}} = {}^0G_{\mathrm{Sb:Te}}^{\mathrm{Sb_2Te_3}} + 1471.4$	11
	$^0L_{\mathrm{Sb:Sb,Te}}^{\mathrm{delta}} = -6394.9 + 12.1759T$	11
	$^1L_{\mathrm{Sb:Sb,Te}}^{\mathrm{delta}} = +1425.0 + 0.9063T$	11
	$^2L_{\mathrm{Sb:Sb,Te}}^{\mathrm{delta}} = -2243.2$	11
PtTe	Model Pt (Sb,Te)	
	$0 < T < 80$	
	$G_{\mathrm{Pt:Te}}^{\mathrm{PtTe}} = -72630.0 - 11.5638T - 0.0017000286T^3 + 5.3633 \times 10^{-6}T^4$	This work
	$T \geq 80$	
	$G_{\mathrm{Pt:Te}}^{\mathrm{PtTe}} = -76497.4 + 223.2802T - 45.9684213T\ln(T) - 0.00975528427T^2$ $+48436.7206T^{-1} + 1.66216155 \times 10^{-6}T^3$	This work
	$G_{\mathrm{Pt:Sb}}^{\mathrm{PtTe}} = G_{\mathrm{Pt:Sb}}^{\mathrm{PtSb}} + 30000.0$	This work
	$^0L_{\mathrm{Pt:Sb,Te}}^{\mathrm{PtTe}} = -1271.7 + 5.5585T$	This work
	$^1L_{\mathrm{Pt:Sb,Te}}^{\mathrm{PtTe}} = +31473.3$	This work

Table II. continued

Phase	Thermodynamic parameters	Ref.
Pt_3Te_4	Model Pt_3 $(Sb,Te)_4$	
	$G_{Pt:Te}^{Pt_3Te_4} = 3GHSER_{Pt} + 4GHSER_{Te} - 247457.0 + 10.7064T$	This work
	$G_{Pt:Sb}^{Pt_3Te_4} = 2G_{Pt:Sb}^{PtSb} + G_{Pt:Sb}^{PtSb_2} + 35000.0$	This work
	$^0L_{Pt:Sb,Te}^{Pt_3Te_4} = -56934.2 + 88.5995T$	This work
Pt_2Te_3	Model Pt_2 $(Sb,Te)_3$	
	$G_{Pt:Te}^{Pt_2Te_3} = 2GHSER_{Pt} + 3GHSER_{Te} - 184917.0 + 10.7101T$	This work
	$G_{Pt:Sb}^{Pt_2Te_3} = G_{Pt:Sb}^{PtSb} + G_{Pt:Sb}^{PtSb_2} + 25000.0$	This work
	$^0L_{Pt:Sb,Te}^{Pt_2Te_3} = -24840.3 + 37.1112T$	This work
$PtTe_2$	Model Pt $(Sb,Te)_2$	
	$0 < T < 80$	
	$G_{Pt:Te}^{PtTe_2} = -134749.3 - 13.4795T - 0.00274613806T^3 + 8.4700 \times 10^{-6}T^4$	This work
	$T \geq 80$	
	$G_{Pt:Te}^{PtTe_2} = -140469.4 + 337.4973T - 68.8581519T\ln(T) - 0.0172150206T^2$	
	$+7.737.708T^{-1} + 3.06779819 \times 10^{-6}T^3$	This work
	$G_{Pt:Sb}^{PtTe_2} = G_{Pt:Sb}^{PtSb_2} + 15000.0$	This work
	$^0L_{Pt:Sb,Te}^{PtTe_2} = -28401.5 + 27.6216T$	This work
	$^1L_{Pt:Sb,Te}^{PtTe_2} = -6724.3$	This work

[a]In J mol^{-1} of the formula units.

Table III. Invariant reactions in the Pt-Te system

	Present work				Kim[6]			
	T (K)	x(Te)			T (K)	x(Te)		
Reaction								
liquid $\rightarrow$ fcc(Pt) + PtTe	1146	0.3630	–	–	1143	0.400		
liquid + Pt_3Te_4 $\rightarrow$ PtTe	1208	0.4342	–	–	1208	–	–	–
liquid + $PtTe_2$ $\rightarrow$ Pt_3Te_4	1290	0.5208	–	–	>1273	0.164	–	–
liquid $\rightarrow$ $PtTe_2$	1423	0.6667	–	–	1423	0.667	–	–
$PtTe_2 + Pt_3Te_4$ $\rightarrow$ Pt_2Te_3	954	–	–	–	923–973	–	–	–
liquid $\rightarrow$ $PtTe_2$ + hex(Te)	720	0.9957	–	–	722	1.000	–	–

Pt-Sb-Te System

In the Pt-Sb-Te system, there are four solution phases: liquid, fcc(Pt), hex(Te), and rhom(Sb). Combining the model of liquid in the Pt-Sb,[13] Sb-Te[11] and Pt-Te systems, the liquid phase in the Pt-Sb-Te system is treated as (Pt, $PtTe_2$, Sb, Sb_2Te_3, Te). The molar Gibbs energy is described by the following expression:

$$G_m^{liquid}(T) = x_{Pt}G_{Pt}^{liquid}(T) + x_{Sb}G_{Sb}^{liquid}(T)$$
$$+ x_{Te}G_{Te}^{liquid}(T) + x_{PtTe_2}G_{PtTe_2}^{liquid}(T)$$
$$+ x_{Sb_2Te_3}G_{Sb_2Te_3}^{liquid}(T) + RT(x_{Pt}\ln x_{Pt}$$
$$+ x_{Sb}\ln x_{Sb} + x_{Te}\ln x_{Te} + x_{PtTe_2}\ln x_{PtTe_2}$$
$$+ x_{Sb_2Te_3}\ln x_{Sb_2Te_3}) + {}^EG_m^{liquid},$$

$$(10)$$

where x_{Pt}, x_{Sb}, x_{PtTe_2}, $x_{Sb_2Te_3}$ and x_{Te} are the mole fractions of Pt, Sb, $PtTe_2$, Sb_2Te_3 and Te, respectively; $^E G_m^{liquid}$ is the excess Gibbs energy composed of binary and ternary excess Gibbs energies and is expressed by the Redlich–Kister polynomial,

$$
\begin{aligned}
^E G_m^{liquid} = {} & x_{Pt} x_{Sb} \sum_j {}^j L_{Pt,Sb}^{liquid} (x_{Pt} - x_{Sb})^j \\
& + x_{Sb} x_{Sb_2Te_3} \sum_j {}^j L_{Sb,Sb_2Te_3}^{liquid} (x_{Sb} - x_{Sb_2Te_3})^j \\
& + x_{Sb_2Te_3} x_{Te} \sum_j {}^j L_{Sb_2Te_3,Te}^{liquid} (x_{Sb_2Te_3} - x_{Te})^j \\
& + x_{Pt} x_{PtTe_2} \sum_j {}^j L_{Pt,PtTe_2}^{liquid} (x_{Pt} - x_{PtTe_2})^j \\
& + x_{PtTe_2} x_{Te} \sum_j {}^j L_{PtTe_2,Te}^{liquid} (x_{PtTe_2} - x_{Te})^j \\
& + x_{PtTe_2} x_{Sb_2Te_3} \, {}^0 L_{PtTe_2,Sb_2Te_3}^{liquid} \\
& + x_{Pt} x_{PtTe_2} x_{Sb} \, {}^0 L_{Pt,PtTe_2,Sb},
\end{aligned}
$$
$$(11)$$

where $^j L_{Pt,Sb}^{liquid}$ is the binary interaction parameter between elements Pt and Sb in liquid in the Pt-Sb system;[13] $^j L_{Sb,Sb_2Te_3}^{liquid}$ and $^j L_{Sb_2Te_3,Te}^{liquid}$ are the interaction parameters of liquid in the Sb-Te system;[11] $^j L_{Pt,PtTe_2}^{liquid}$ and $^j L_{PtTe_2,Te}^{liquid}$ are interaction parameters of liquid in the Pt-Te system, which are to be optimized in the present work. $^0 L_{PtTe_2,Sb_2Te_3}^{liquid}$ and $^0 L_{Pt,PtTe_2,Sb}^{liquid}$ are the ternary interaction parameters to be optimized according to the phase equilibria of liquid at different isothermal sections.[3,16,17]

The solution phases fcc(Pt), hex(Te), and rhom(Sb) are treated as a substitutional solution, and the expression of the molar Gibbs energy is similar to Eq. (2) in Ref. 13.

The compounds, $PtTe_2$, Pt_2Te_3, Pt_3Te_4 and PtTe in the Pt-Te system and $PtSb_2$, PtSb, Pt_3Sb_2 and Pt_7Sb in the Pt-Sb system, with a solid solubility of the third elements, are treated as line compounds $Pt_m(Sb,Te)_n$. The molar Gibbs energy of each of these compounds is expressed as follows,

$$
\begin{aligned}
G_m^\phi = {} & y_{Sb} G_{Pt:Sb}^\phi + y_{Te} G_{Pt:Te}^\phi \\
& + nRT (y_{Sb} \ln y_{Sb} + y_{Te} \ln y_{Te}) \\
& + y_{Sb} y_{Te} \sum_j {}^j L_{Pt:Sb,Te}^\phi (y_{Sb} - y_{Te})^j
\end{aligned}
$$
$$(12)$$

The compound Pt_5Sb with a homogeneity range in the Pt-Sb system was treated as $(Pt,Sb)_5(Pt,Sb)$ by a two-sublattice model[19,20] in Ref. 13 The solubility of Te in Pt_5Sb is about ~1 at.%,[3] and it is described as $(Pt\%,Sb)_5(Pt,Sb\%,Te)$ in the Pt-Sb-Te system.

ASSESSMENT PROCEDURE

In order to model the Pt-Sb-Te system, the thermodynamic parameters of the Pt-Sb, Sb-Te, and Pt-Te binary systems should be obtained. Those of the Sb-Te and Pt-Sb systems are taken from Refs. 11 and 13, respectively, and the calculated Sb-Te and Pt-Sb phase diagrams are shown in Figs. 1 and 2. Due to the lack of experimental measurements for Pt_2Te_3 and Pt_3Te_4 in the Pt-Te system, the enthalpies of the formation of Pt_2Te_3 and Pt_3Te_4, as well as $PtTe_2$ and PtTe, are calculated in the present work by means of first-principles calculations. The process of obtaining enthalpies of formation of compounds using first-principles calculations is described in Ref. 13.
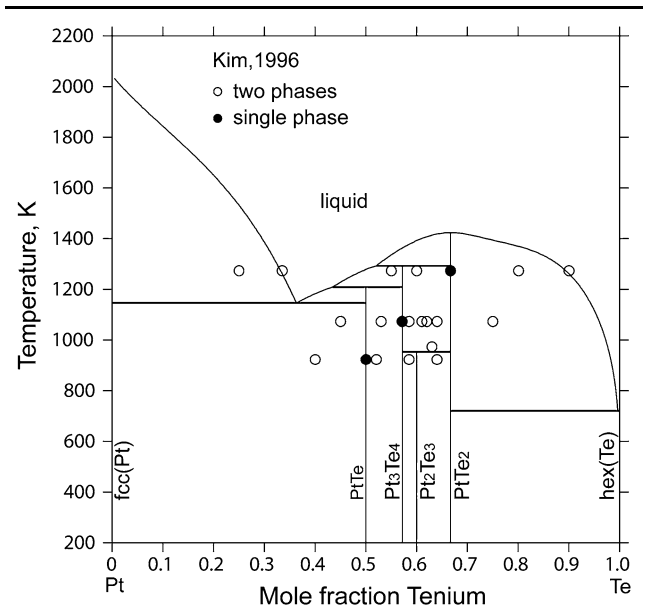

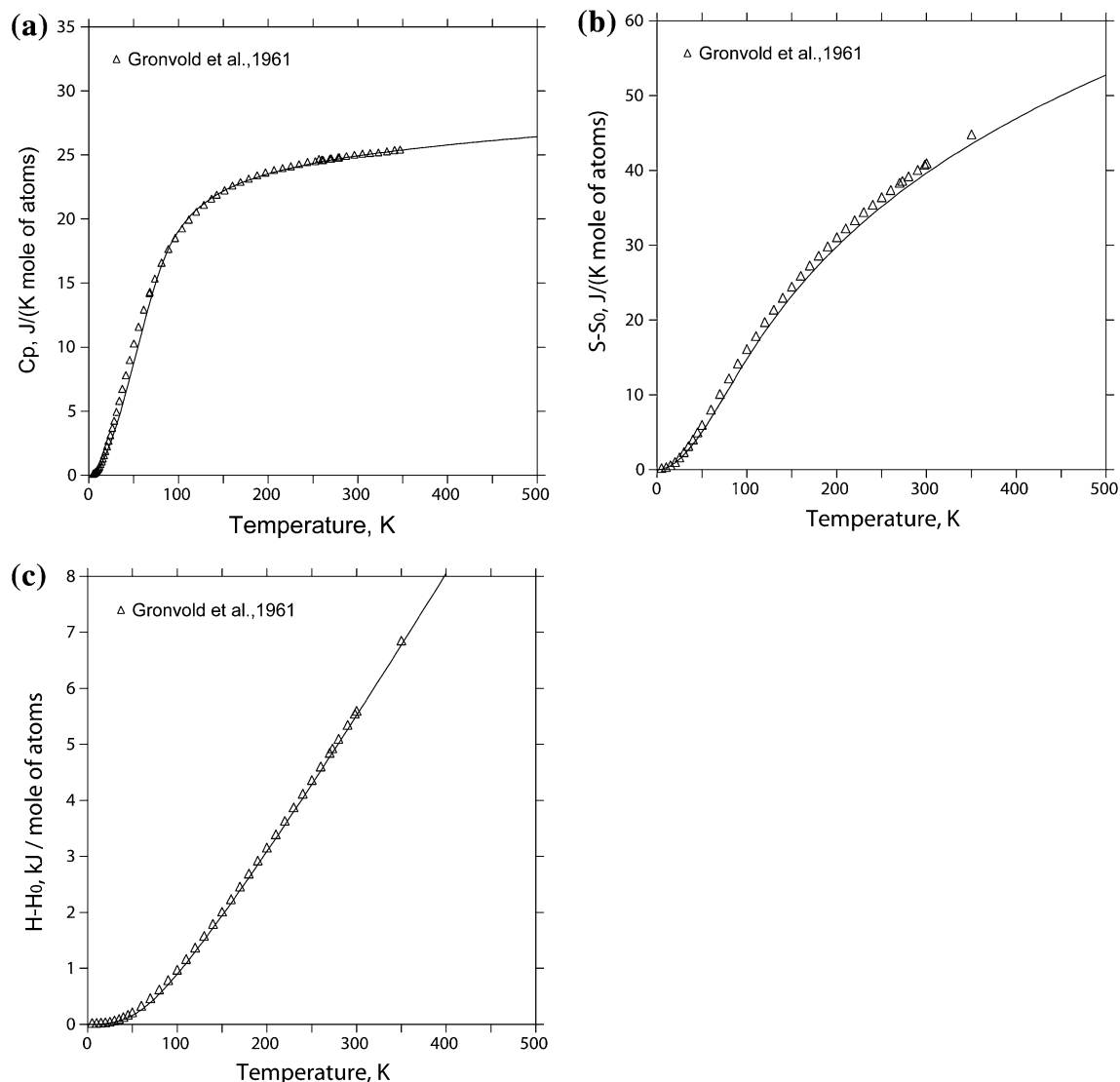Fig. 3. Calculated Pt-Te phase diagram in comparison with the experimental data[6].

(a)

(b)

(c)

Fig. 4. Calculated thermochemical properties of PtTe with the experimental data.[8] (a) Cp, (b) S-S$_0$, (c) H-H$_0$.

The space group, atoms per primitive cell, and the k-point mesh used for Pt, Te, PtTe$_2$, Pt$_2$Te$_3$, Pt$_3$Te$_4$ and PtTe, and the latest experimental lattice parameters[3,16,21–23] are listed in Table I.

The optimization is carried out by means of the optimization module PARROT of the thermodynamic software Thermo-Calc,[24] which can handle various kinds of experimental data. Before optimizing the Pt-Sb-Te ternary system, the Pt-Te system is optimized based on the experimental data in Refs. 4–6.

During the optimization procedure, the experimental data of the Pt-Te phase diagram in Ref. 6 is given a larger weight. The experimental
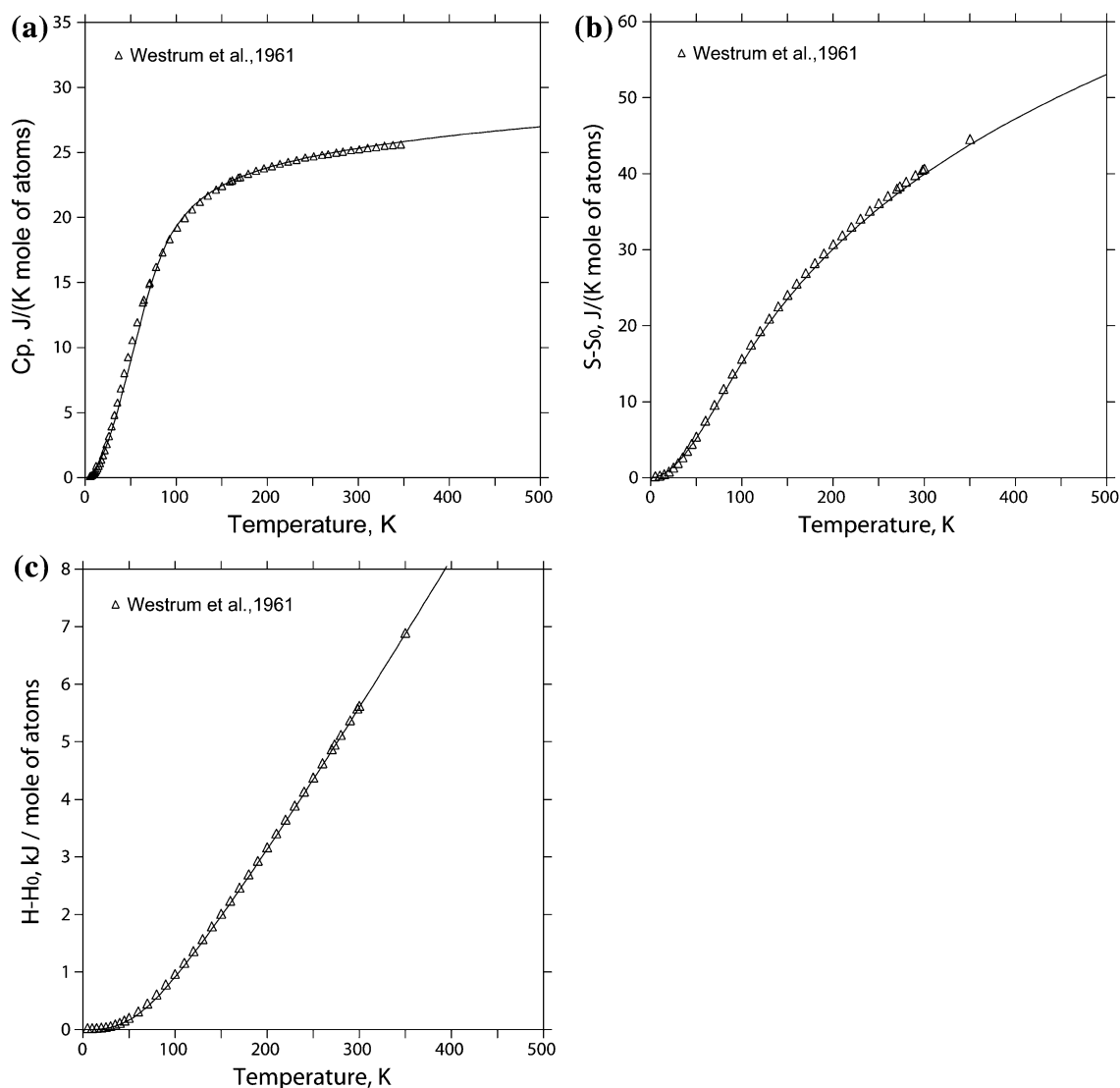
Fig. 5. Calculated thermochemical properties of PtTe$_2$ with the experimental data.[9] (a) Cp, (b) S-S$_0$, (c) H-H$_0$.

heat capacities measured by Grønvold et al.[8] and Westrum et al.[9] are used to optimize the thermo-dynamic parameters of PtTe and PtTe$_2$, respective-ly. As for the formation enthalpies of compounds in the Pt-Te system, the values calculated from first-principles calculations are used as the starting values at the beginning of the optimization. Then,

thermodynamic parameters of compounds are opti-mized to fit the experimental phase equilibria.[4–6]

As for the Pt-Sb-Te ternary system, three isother-mal sections at 873 K,[3] 1073 K[16] and 1273[17] K are given larger weight during the optimization, while the part between 0 at.% and 33 at.% Pt of the isothermal section at 923 K is not considered

in the present work because its phase relationships in the Sb-Te binary terminal adopted by El-Boragy and Schubert[14] is inconsistent with the phase diagram assessed by Ghosh et al.[10] and Guo et al.[11]

The thermodynamic descriptions of liquid, fcc(Pt), rhom(Sb) and hex(Te) in the Pt-Sb-Te system are obtained by combining the corresponding Gibbs energy functions from the assessments of the binary systems using Muggianu interpolation for excess terms.[25] In the present work, the coefficients $^0L^{\text{liquid}}_{\text{PtTe}_2,\text{Sb}_2\text{Pt}_3}$ and $^0L^{\text{liquid}}_{\text{Pt},\text{PtTe}_2,\text{Sb}}$ are optimized on the basis of the phase relationships related to liquid in isothermal sections determined by Kim.[3,16,17]

For the compounds PtTe_2, Pt_2Te_3, Pt_3Te_4, PtTe, PtSb_2, PtSb, Pt_3Sb_2, Pt_5Sb and Pt_7Sb in the Pt-Sb-Te system, the thermodynamic parameters are optimized according to the experimental data.[3,14,16,17] The assessment procedure is similar to that for treating the C40 compound in Ref. [26].

RESULTS AND DISCUSSIONS

Figures 1 and 2 are the calculated Sb-Te and Pt-Sb phase diagrams using the thermodynamic parameters from Refs. [11] and [13], respectively.

The thermodynamic parameters of the Pt-Te and Pt-Sb-Te systems obtained in the present work are shown in Table II. The liquid phase is described using the associate model. Table III shows the calculated invariant reactions in the Pt-Te system. It can be seen by comparison that the experimental temperatures and compositions for the invariant reactions are well reproduced.

Figure 3 is the calculated Pt-Te phase diagram using the present thermodynamic parameters, which is basically consistent with the experimental data.[6] Figures 4a–c and 5a–c show the calculated Cp, S-S_0 and H-H_0 of PtTe and PtTe_2, respectively, in comparison with the experimental data.[8,9] As shown in Figs. 4 and 5, the calculated results are consistent with the experimental data. Figure 6 shows the calculated enthalpies of the formation of the compounds PtTe_2, Pt_2Te_3, Pt_3Te_4 and PtTe in comparison with the values from first-principles calculations and the calculated value from Ref. [7]. In Fig. 6, the values from the first-principles calculations are reproduced well.

Figure 7a–d are the calculated isothermal sections at 873, 923, 1073 and 1273 K, respectively. Comparing the three-phase region PtSb + PtSb_2 + PtTe_2

at 873, 923, 1073 and 1273 K, the experimental equilibrium compositions of PtSb_2 at 923, 1073 and 1273 K are more reasonable than the one at 873 K when PtSb_2 is treated as a linear compound. Therefore, two experimental alloys with the compositions of 39.97 Pt + 55.03 Sb + 5.00 Te and 40.03 Pt + 49.98 Sb + 9.98 Te (at.%)[3] are not included in the three-phase region of PtSb + PtSb_2 + PtTe_2 at 873 K. The other two Te-rich experimental data with the compositions of 37.00 Pt + 57.00 Te + 6.00 Sb and 20.00 Pt + 19.99 Sb + 60.01 Te (at.%) are not included in the three-phase regions of PtSb_2 + PtTe_2 + Pt_2Te_3 and PtSb_2 + PtTe_2 + liquid at 873 K, respectively. If these two experimental data are reproduced in the calculated results, several four-phase invariant reactions would occur at about 673 K. Considering that the solid state phase transformation is very difficult at low temperature due to the low atomic diffusion ability, the above two experimental data are not reproduced in the present work in order to make sure that the phase relationships in the temperature range between 300 K and 873 K are unchanged.

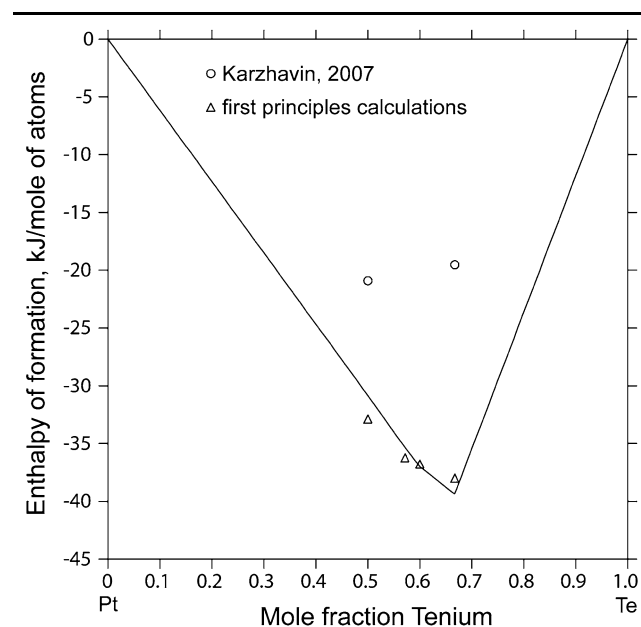Figure 8 is the predicted liquidus projection of the Pt-Sb-Te system. As shown in Fig. 8a, the liquidus

Fig. 6. Calculated enthalpy of formation in the Pt-Te system at 298 K in comparison with the calculated results of Karzhavin[7] and from first-principles calculations in the present work.
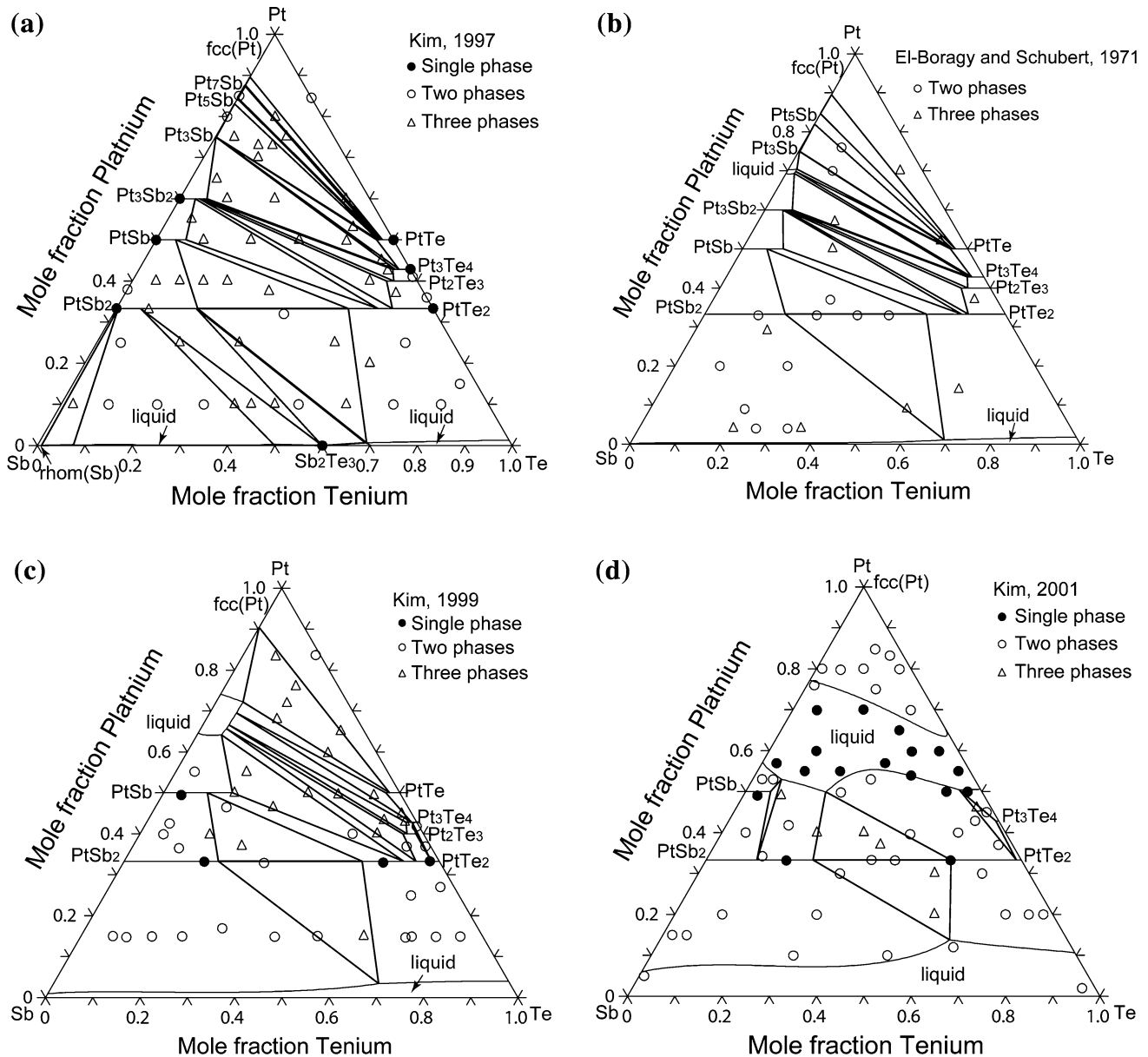
Fig. 7. Calculated isothermal sections of the Pt-Sb-Te system using the present thermodynamic description. (a) 873 K with the experimental data from Ref. 3, (b) 923 K with the experimental data from Ref. 14, (c) 1073 K with the experimental data from Ref. 16, (d) 1273 K with the experimental data from Ref. 17.

surface of Pt$_2$Te$_3$ occurs in the liquidus projection because Pt$_2$Te$_3$ becomes stable at high temperature with the addition of Sb, which can be seen in the isothermal section at 1073 K. Table IV shows the predicted invariant reactions in the Pt-Sb-Te system.
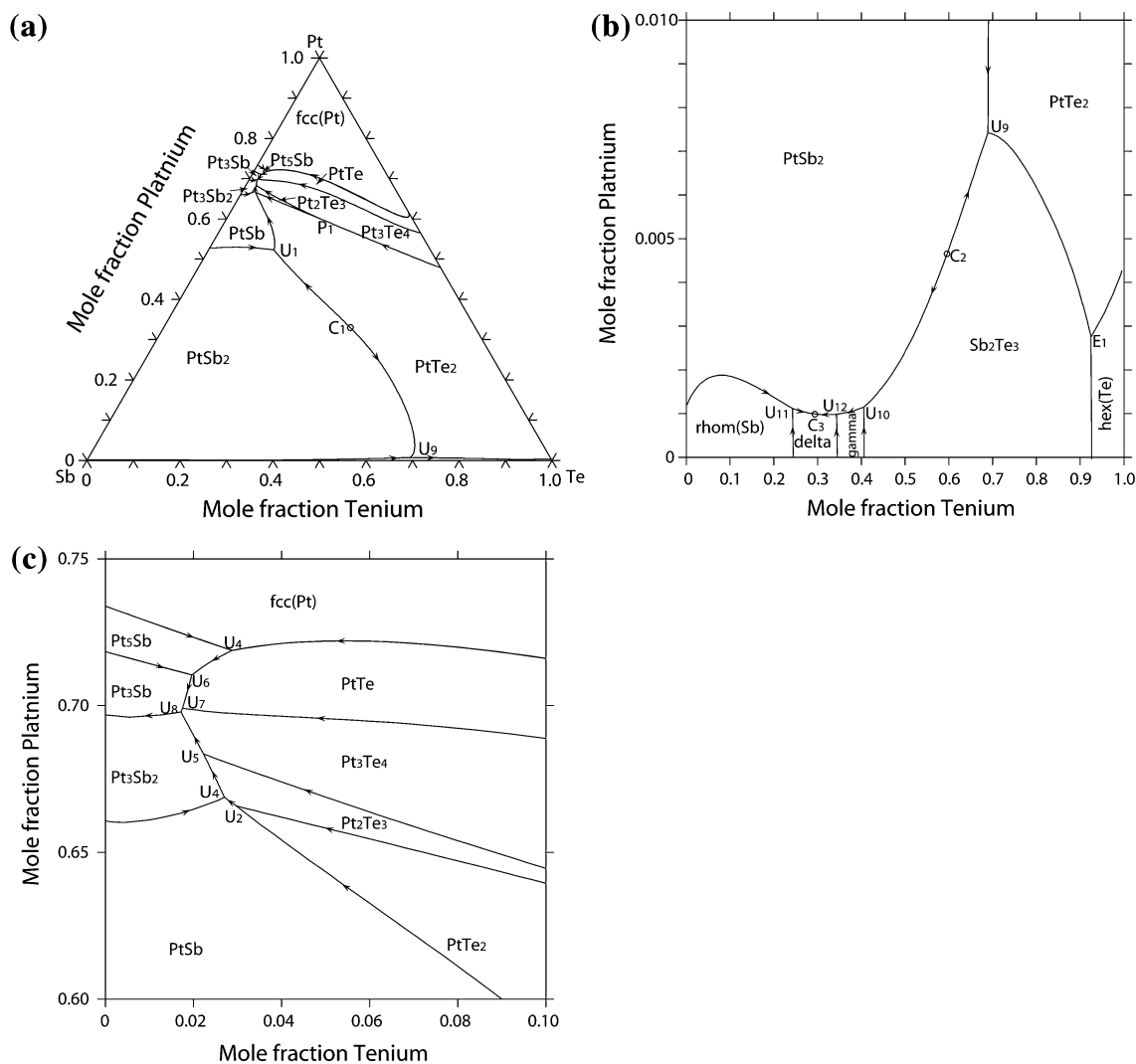
Fig. 8. (a) Predicted liquidus projection of the Pt-Sb-Te system using the present thermodynamic description. (b) Enlarged section of (a) in the rich Sb-Te side, (c) Enlarged section of (a) in the rich Pt-Sb side.

CONCLUSIONS

The phase relationships of the Pt-Te and Pt-Sb-Te systems, thermodynamic parameters Cp, S-S$_0$, and H-H$_0$, of PtTe and PtTe$_2$ 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 Pt-Sb-Te system as the functions of composition and temperature is obtained. With the present optimized parameters, various thermodynamic calculations of practical interest can be made.

Table IV. Invariant reactions in the Pt-Sb-Te system

Reaction	Present work					
	Type	T (K)	x(Pt)	x(Sb)	x(Te)
liquid + $PtTe_2$ + $PtSb_2$	C_1	1354	0.3361	0.2689	0.4005
liquid + $PtSb_2$ + Sb_2Te_3	C_2	890	0.0043	0.4013	0.5944
liquid + $PtSb_2$ + delta	C_3	817	0.0010	0.7049	0.2942
liquid + Pt_3Te_4 + $PtTe_2$ $\rightarrow$ Pt_2Te_3	P_1	1230	0.6006	0.1982	0.2012
liquid + $PtSb_2$ $\rightarrow$ PtSb + $PtTe_2$	U_1	1246	0.5232	0.3361	0.1407
liquid + $PtTe_2$ $\rightarrow$ Pt_2Te_3 + PtSb	U_2	989	0.6658	0.3045	0.0297
liquid +fcc $\rightarrow$ PtTe + Pt_5Sb	U_3	982	0.7187	0.2525	0.0288
liquid + PtSb $\rightarrow$ Pt_2Te_3 + Pt_3Sb_2	U_4	976	0.6687	0.3042	0.0270
liquid + Pt_2Te_3 $\rightarrow$ Pt_3Sb_2 + Pt_3Te_4	U_5	947	0.6835	0.2942	0.0223
liquid + Pt_5Sb $\rightarrow$ PtTe + Pt_3Sb	U_6	931	0.7104	0.2700	0.0196
liquid + PtTe $\rightarrow$ Pt_3Te_4 + Pt_3Sb	U_7	914	0.6991	0.2834	0.0175
liquid + Pt_3Te_4 $\rightarrow$ Pt_3Sb + Pt_3Sb_2	U_8	913	0.6978	0.2851	0.0172
liquid + $PtSb_2$ $\rightarrow$ $PtTe_2$ + Sb_2Te_3	U_9	872	0.0068	0.3035	0.6897
liquid + Sb_2Te_3 $\rightarrow$ $PtSb_2$ + Gamma	U_{10}	831	0.0011	0.5933	0.4056
liquid +rhom(Sb) $\rightarrow$ $PtSb_2$ +delta	U_{11}	821	0.0011	0.7561	0.2428
liquid + gamma $\rightarrow$ $PtSb_2$ + delta	U_{12}	820	0.0010	0.6556	0.3434
liquid $\rightarrow$ $PtTe_2$ +Sb_2Te_3 + hex(Te)	E_1	687	0.0024	0.0726	0.9250

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