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Thermodynamic optimization of the Ge–Sb and Ge–Sb–Sn systems

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ABSTRACT

The thermodynamic modeling and optimization of the Ge–Sb and Ge–Sb–Sn systems were critically carried out by means of the CALPHAD (CALculation of PHAse Diagram) technique. The solution phases, liquid, diamond, bct and rhombohedral, were described by the substitutional solution model. The compound SbSn was treated as the formulae $(Ge,Sb,Sn)_1(Ge,Sb,Sn)_1$ in the Ge–Sb–Sn system. A self-consistent thermodynamic description of the Ge–Sb–Sn system was developed. Three isothermal sections at 692, 594 and 518 K, the projection of the liquidus surfaces, and the complete reaction scheme for the Ge–Sb–Sn system in the literature were reproduced.

1. Introduction

Germanium based alloys materials have gained increasing attention in recent years because of its potential application as Ge–Sb–Sn–O (GSSO) inorganic resistance materials formed by thermal lithography [1], as amorphous Ge alloy films [2] and as Ge–Sb–Te and Bi–Ge–Sb–Sn–Te phase-change recording films [3,4]. To be a good candidate, the alloy must exhibit good thermal stability and avoid phase segregation after recording or erasing cycles. Thus, to obtain the thermodynamic properties of the alloys is of importance. In this work, the Ge–Sb and the Ge–Sb–Sn systems are optimized by means of the CALculation of PHAse Diagram (CALPHAD) technique.

2. Literature information

2.1. The Ge–Sb system

The phase diagram of the Ge–Sb system is a simple eutectic system. The liquidus has been investigated by Stöhr and Klemm [5], Ruttewit and Masing [6], Zhurikin et al. [7], Malmejac et al. [8] and Alfer et al. [9]. The experimental data determined by Refs. [5–9] were generally consistent with each other. A very small solubility of Sb in the diamond was determined by Zhurikin et al. [7], Trumbore [10], Trumbore et al. [11], Akopyan and Abdullayev [12] and Glazov and Abdullyev [13]. Olesinski and Abbaschian [14] reviewed the Ge–Sb system on the basis of the information [5–13] and recommended the temperature and composition of liquid in the eutectic reaction at 865 K and 85.5 at.% Sb. And the Ge–Sb system was optimized later by Chevalier [15].

The activities of Ge and Sb in liquid at 1073, 1173 and 1273 K were measured by Kostov et al. [16]. The enthalpy of mixing of liquid at 1250 and 1273 K was determined by Predel and Stein [17] and Alfer et al. [18], respectively.

The Ge–Sb system was optimized by Wang et al. [19], regarding to the experimental information [5–18]. More recently, the Ge–Sb system was reinvestigated by Nasir et al. [20]. Comparing with the literature [5,6,14,15,19], the main difference is the temperature and composition of the invariant reaction liquid → diamond + rhom, in which the reaction temperature is 860 and 865 K, the composition of liquid is 85.7 and 77.5 at.% Sb, and the maximal solid solubility value of Ge in the rhombohedral phase is 0 and 6.3 at.% in Refs. [19,20], respectively.

On the basis of the phase diagram reinvestigated by Nasir et al. [20] and the thermochemical data [16–18], the Ge–Sb system was re-optimized in this work.

2.2. The Ge–Sn system

The Ge–Sn system has been compiled by Olesinski and Abbaschian [21] and well optimized by Feutelais et al. [22]. The thermodynamic parameters obtained by Feutelais et al. [22] were adopted in the present work, and the calculated phase diagram was shown in Fig. 1.

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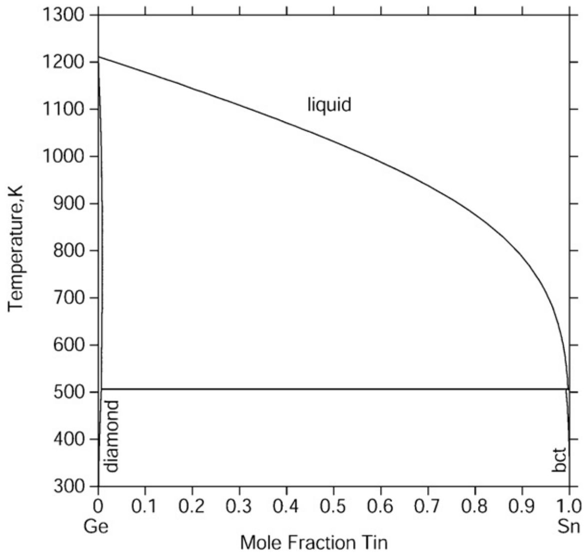

Fig. 1. Calculated Ge–Sn phase diagram by Feutelais et al. [22].

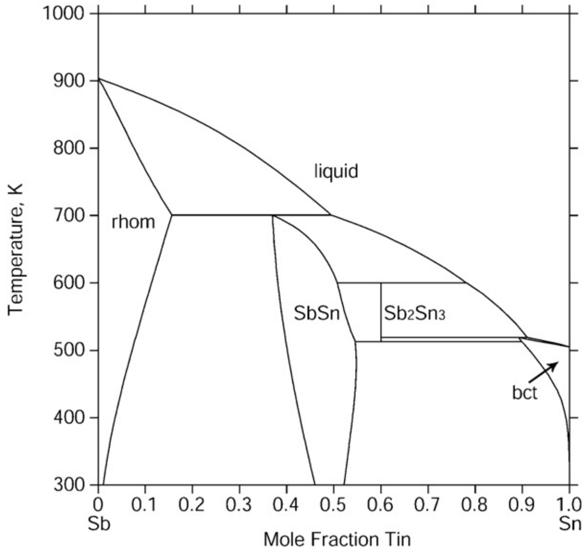

Fig. 2. Calculated Sb–Sn phase diagram by Kroupa and Vízdal [26].

2.3. The Sb–Sn system

The available experimental information for the Sb–Sn system was reviewed by Romanowska [23] and Manasijevic et al. [24]. Jǒnsson and Ågren [25] performed the first thermodynamic assessment of the Sb–Sn system. Later, the Sb–Sn system was re-optimized by Kroupa and Vízdal [26] on the basis of the new experimental data of Vassiliev et al. [27]. The thermodynamic parameters obtained by Kroupa and Vízdal [26] were adopted in the present work, and the calculated phase diagram was shown in Fig. 2.

2.4. The Ge–Sb–Sn system

Gubenko and Miller [28] investigated the partial vertical sections at Ge–(Sn + 2 wt.% Sb) and Ge–(Sn + 5.5 wt.% Sb). Kuznetsov et al. [29] determined the vertical section at Ge–(Sn + 29.5 at.% Sb), a part of the Ge-side solidus surface (to 1 at.% Sn and 0.06 at.% Sb) and the partial liquidus surface (0–60 at.% Ge).

The detailed investigation of the Ge–Sb–Sn system were done by Dichi et al. [30], who determined three isothermal sections at 692, 594 and 518 K, two vertical sections at 10 at.% and 20 at.% Ge, the projection of liquidus surfaces, and presented the complete reaction scheme. The experimental data reported by Dichi et al. [30] was mainly considered in this optimization.

3. Thermodynamic models and assessment procedure

3.1. Unary phases

The Gibbs energy function $G_i^\phi(T) = {}^0G_i^\phi(T) - H_i^{\mathrm{SER}}$ (298.15 K) for the element i (i = Ge, Sb, Sn) in the phase ϕ (ϕ = liquid, diamond, rhom, or bct) is described as follows

$$G_i^\phi(T) = a + bT + cT\ln T + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9} \tag{1}$$

where H_i^{SER} (298.15 K) is the molar enthalpy of the element i at 298.15 K in its standard element reference (SER) state, diamond for Ge, rhombohedral for Sb and bct for Sn. The Gibbs energy of the element i, $G_i^\phi(T)$, in its SER state, is denoted by GHSER$_i$, i.e.,

$$\mathrm{GHSER}_i = {}^0G_i^\phi(T) - H_i^{\mathrm{SER}} \quad (298.15\,\mathrm{K}) \tag{2}$$

In the present work, the Gibbs energy functions are taken from the SGTE (Scientific Group of Thermodata Europe) pure elements database compiled by Dinsdale [31] and listed in Table 1.

3.2. Solution phases

In the Ge–Sb–Sn system, there are four solution phases, liquid, diamond, rhombohedral, and bct. Their molar Gibbs energies are described by the following expression:

$$\begin{aligned} G_{\mathrm{m}}^\phi &= x_{\mathrm{Ge}}G_{\mathrm{Ge}}^\phi(T) + x_{\mathrm{Sb}}G_{\mathrm{Sb}}^\phi(T) + x_{\mathrm{Sn}}G_{\mathrm{Sn}}^\phi(T) + RT(x_{\mathrm{Ge}}\ln x_{\mathrm{Ge}} \\ &\quad + x_{\mathrm{Sb}}\ln x_{\mathrm{Sb}} + x_{\mathrm{Sn}}\ln x_{\mathrm{Sn}}) + {}^EG_m^\phi \end{aligned} \tag{3}$$

where R is the gas constant; x_{Ge}, x_{Sb} and x_{Sn} are the mole fractions of the pure elements Ge, Sb and Sn, respectively; ${}^EG_m^\phi$ is the excess Gibbs energy, expressed by the Redlich–Kister polynomial [32].

$$\begin{aligned} {}^EG_m^\phi &= x_{\mathrm{Ge}}x_{\mathrm{Sb}}\sum_j {}^jL_{\mathrm{Ge,Sb}}^\phi(x_{\mathrm{Ge}} - x_{\mathrm{Sb}})^j + x_{\mathrm{Ge}}x_{\mathrm{Sn}}\sum_j {}^jL_{\mathrm{Ge,Sn}}^\phi(x_{\mathrm{Ge}} - x_{\mathrm{Sn}})^j \\ &\quad + x_{\mathrm{Sb}}x_{\mathrm{Sn}}\sum_j {}^jL_{\mathrm{Sb,Sn}}^\phi(x_{\mathrm{Sb}} - x_{\mathrm{Sn}})^j + x_{\mathrm{Ge}}x_{\mathrm{Sb}}x_{\mathrm{Sn}}L_{\mathrm{Ge,Sb,Sn}}^\phi \end{aligned} \tag{4}$$

where ${}^jL_{\mathrm{Ge,Sb}}^\phi$, ${}^jL_{\mathrm{Ge,Sn}}^\phi$ and ${}^jL_{\mathrm{Sb,Sn}}^\phi$ are the binary interaction parameters between elements Ge and Sb, Ge and Sn, and Sb and Sn, respectively. Its general form is

$$L^\phi = a + bT + cT\ln T + dT^2 + eT^3 + fT^{-1} \tag{5}$$

but in most case only the first one or two terms are used according to the temperature dependence of the experimental data. $L_{\mathrm{Ge,Sb,Sn}}^\phi$ is the ternary interaction parameter expressed as:

$$L_{\mathrm{Ge,Sb,Sn}}^\phi = x_{\mathrm{Ge}}\,{}^0L_{\mathrm{Ge,Sb,Sn}}^\phi + x_{\mathrm{Sb}}\,{}^1L_{\mathrm{Ge,Sb,Sn}}^\phi + x_{\mathrm{Sn}}\,{}^2L_{\mathrm{Ge,Sb,Sn}}^\phi \tag{6}$$

where ${}^jL_{\mathrm{Ge,Sb,Sn}}^\phi = a_j + b_jT$ (j = 0, 1, 2). a_j and b_j are the parameters to be optimized in this work.

Table 1
Thermodynamic parameters of the Ge–Sb–Sn system.[a]

Phase	Temperature (K)	Thermodynamic parameters	Reference
	298.15–900	$\mathrm{GHSER_{Ge}} = -9486.153 + 165.635573T - 29.5337682T\ln(T) + 5.568297 \times 10^{-3}T^2 - 1.513694 \times 10^{-6}T^3 + 163298T^{-1}$	[31]
	900–1211.40	$\mathrm{GHSER_{Ge}} = -5689.239 + 102.86087T - 19.8536239T\ln(T) - 3.672527 \times 10^{-3}T^2$	
	1211.40–3200	$\mathrm{GHSER_{Ge}} = -9548.204 + 156.708024T - 27.6144T\ln(T) - 8.59809 \times 10^{28}T^{-9}$	
	298.15–903.78	$\mathrm{GHSER_{Sb}} = -9242.858 + 156.154689T - 30.5130752T\ln(T) + 7.748768 \times 10^{-3}T^2 - 3.003415 \times 10^{-6}T^3 + 100625T^{-1}$	[31]
	903.78–2000	$\mathrm{GHSER_{Sb}} = -11738.83 + 169.485872T - 31.38T\ln(T) + 1616.8491024T^{-9}$	
	100–250	$\mathrm{GHSER_{Sn}} = -7958.517 + 122.765451T - 25.858T\ln(T) + 0.51185 \times 10^{-3}T^2 - 3.192767 \times 10^{-6}T^3 + 18440T^{-1}$	[31]
	250–505.08	$\mathrm{GHSER_{Sn}} = -5855.135 + 65.443315T - 15.961T\ln(T) - 18.8702 \times 10^{-3}T^2 + 3.121167 \times 10^{-6}T^3 - 61960T^{-1}$	
	505.08–800	$\mathrm{GHSER_{Sn}} = +2524.724 + 4.005269T - 8.2590486T\ln(T) - 16.814429 \times 10^{-3}T^2 + 2.623131 \times 10^{-6}T^3 - 1081244T^{-1} - 1.2307 \times 10^{25}T^{-9}$	
	800–3000	$\mathrm{GHSER_{Sn}} = -8256.959 + 138.99688T - 28.4512T\ln(T) - 1.2307 \times 10^{25}T^{-9}$	
Liquid		Model: $(\mathrm{Ge, Sb,Sn})_1$	
	298.14–900	$G(\mathrm{liquid, Ge}) = +27655.337 + 134.94853T - 29.5337682T\ln(T) + 0.005568297T^2 - 1.513694 \times 10^{-6}T^3 + 163298T^{-1} + 8.56632 \times 10^{-21}T^7$	[31]
	900–1211.4	$G(\mathrm{liquid, Ge}) = +31452.25 + 72.173826T - 19.8536239T\ln(T) - 0.003672527T^2 + 8.56632 \times 10^{-21}T^7$	
	1211.40–3200	$G(\mathrm{liquid, Ge}) = +27243.473 + 126.324186T - 27.6144T\ln(T)$	
	298.14–903.78	$G(\mathrm{liquid, Sb}) = +10579.47 + 134.231525T - 30.5130752T\ln(T) + 0.007748768T^2 - 3.003415 \times 10^{-6}T^3 + 100625T^{-1} - 1.74847 \times 10^{-20}T^7$	[31]
	903.78–2000	$G(\mathrm{liquid, Sb}) = +8175.359 + 147.455986T - 31.38T\ln(T)$	
	100–250	$G(\mathrm{liquid, Sn}) = -855.425 + 108.677684T - 25.858T\ln(T) + 5.1185 \times 10^{-4}T^2 - 3.192767 \times 10^{-6}T^3 + 18440T^{-1} + 1.47031 \times 10^{-18}T^7$	[31]
	250–505.08	$G(\mathrm{liquid, Sn}) = +1247.957 + 51.355548T - 15.961T\ln(T) - 0.0188702T^2 + 3.121167 \times 10^{-6}T^3 - 61960T^{-1} + 1.47031 \times 10^{-18}T^7$	
	505–800	$G(\mathrm{liquid, Sn}) = +9496.31 - 9.809114T - 8.2590486T\ln(T) - 0.016814429T^2 + 2.623131 \times 10^{-6}T^3 - 1081244T^{-1}$	
	800–3000	$G(\mathrm{liquid, Sn}) = -1285.372 + 125.182498T - 28.4512T\ln(T)$	
		${}^{0}L^{\mathrm{liq.}}_{\mathrm{Ge,Sb}} = +3289.7 - 0.5212T$	This work
		${}^{0}L^{\mathrm{liq.}}_{\mathrm{Ge,Sn}} = +2738.5 - 0.7278T$	[22]
		${}^{1}L^{\mathrm{liq.}}_{\mathrm{Ge,Sn}} = -472.4$	[22]
		${}^{0}L^{\mathrm{liq.}}_{\mathrm{Sb,Sn}} = -5695.1 - 1.7090T$	[26]
		${}^{1}L^{\mathrm{liq.}}_{\mathrm{Sb,Sn}} = +782.6$	[26]
		${}^{2}L^{\mathrm{liq.}}_{\mathrm{Sb,Sn}} = +1840.9$	[26]
		${}^{0}L^{\mathrm{liq.}}_{\mathrm{Ge,Sb,Sn}} = -12521.6 + 13.0000T$	This work
		${}^{1}L^{\mathrm{liq.}}_{\mathrm{Ge,Sb,Sn}} = -37997.8 + 42.5440T$	This work
		${}^{2}L^{\mathrm{liq.}}_{\mathrm{Ge,Sb,Sn}} = +31152.9 - 8.0000T$	This work
Diamond		Model: $(\mathrm{Ge, Sb,Sn})_1$	
	298.14–3200	$G(\mathrm{diamond, Ge}) = +\mathrm{GHSER_{Ge}}$	[31]
		$G(\mathrm{diamond, Sb}) = +\mathrm{GHSER_{Sb}} + 5000.0$	This work
	100–298.14	$G(\mathrm{diamond, Sn}) = -9579.608 + 114.007785T - 22.972T\ln(T) - 0.00813975T^2 + 2.7288 \times 10^{-6}T^3 + 25615T^{-1}$	[31]
	298.14–800	$G(\mathrm{diamond, Sn}) = -9063.001 + 104.84654T - 21.5750771T\ln(T) - 0.008575282T^2 + 1.784447 \times 10^{-6}T^3 - 2544T^{-1}$	
	800–3000	$G(\mathrm{diamond, Sn}) = -10909.351 + 147.396535T - 28.4512T\ln(T)$	
		${}^{0}L^{\mathrm{diamond}}_{\mathrm{Ge,Sb}} = +79210.1 - 19.8000T$	[19]
		${}^{0}L^{\mathrm{diamond}}_{\mathrm{Ge,Sn}} = +14471.1 + 10.6195T$	[22]
		${}^{0}L^{\mathrm{diamond}}_{\mathrm{Ge,Sb,Sn}} = 0.0$	This work
		${}^{1}L^{\mathrm{diamond}}_{\mathrm{Ge,Sb,Sn}} = 0.0$	This work
		${}^{2}L^{\mathrm{diamond}}_{\mathrm{Ge,Sb,Sn}} = 0.0$	This work

rhom		Model: $(\mathrm{Ge, Sb,Sn})_1$	
	298.14–900	$G(\mathrm{rhom, Ge}) = +20313.847 + 149.135573T - 29.5337682T\ln(T) + 0.005568297T^2 - 1.513694 \times 10^{-6}T^3 + 163298T^{-1}$	[31]
	900–1211.4	$G(\mathrm{rhom, Ge}) = +24110.761 + 86.36087T - 19.8536239T\ln(T) - 0.003672527T^2$	
	1211.4–3000	$G(\mathrm{rhom, Ge}) = +20251.796 + 140.208024T - 27.6144T\ln(T) - 8.59809 \times 10^{28}T^{-9}$	
	298.14–2000	$G(\mathrm{rhom, Sb}) = +\mathrm{GHSER_{Sb}}$	[31]
	100–250	$G(\mathrm{rhom, Sn}) = -5923.517 + 122.765451T - 25.858T\ln(T) + 5.1185 \times 10^{-4}T^2 - 3.192767 \times 10^{-6}T^3 + 18440T^{-1}$	[31]
	250–505.08	$G(\mathrm{rhom, Sn}) = -3820.135 + 65.443315T - 15.961T\ln(T) - 0.0188702T^2 + 3.121167 \times 10^{-6}T^3 - 61960T^{-1}$	
	505.08–800	$G(\mathrm{rhom, Sn}) = +4559.724 + 4.005269T - 8.2590486T\ln(T) - 0.016814429T^2 + 2.623131 \times 10^{-6}T^3 - 1081244T^{-1} - 1.2307 \times 10^{25}T^{-9}$	
	800–3000	$G(\mathrm{rhom, Sn}) = -6221.959 + 138.99688T - 28.4512T\ln(T) - 1.2307 \times 10^{25}T^{-9}$	
		${}^{0}L^{\mathrm{rhom}}_{\mathrm{Ge,Sb}} = +10695.0 - 6.5572T$	This work
		${}^{0}L^{\mathrm{rhom}}_{\mathrm{Sb,Sn}} = +4000.0 - 5.7323T$	[26]
		${}^{0}L^{\mathrm{rhom}}_{\mathrm{Ge,Sb,Sn}} = +30429.2$	This work
		${}^{1}L^{\mathrm{rhom}}_{\mathrm{Ge,Sb,Sn}} = +31426.1$	This work
		${}^{2}L^{\mathrm{rhom}}_{\mathrm{Ge,Sb,Sn}} = +31748.8$	This work
bct		Model: $(\mathrm{Ge, Sb,Sn})_1$	
	298.14–900	$G(\mathrm{bct, Ge}) = +19313.847 + 149.135573T - 29.5337682T\ln(T) + 0.005568297T^2 - 1.513694 \times 10^{-6}T^3 + 163298T^{-1}$	[31]
	900–1211.4	$G(\mathrm{bct, Ge}) = +23110.761 + 86.36087T - 19.8536239T\ln(T) - 0.003672527T^2$	
	1211.4–3000	$G(\mathrm{bct, Ge}) = +19251.796 + 140.208024T - 27.6144T\ln(T) - 8.59809 \times 10^{28}T^{-9}$	
	298.14–903.78	$G(\mathrm{bct, Sb}) = +3757.142 + 148.154689T - 30.5130752T\ln(T) + 0.007748768T^2 - 3.003415 \times 10^{-6}T^3 + 100625T^{-1}$	[31]
	903.78–2000	$G(\mathrm{bct, Sb}) = +1261.17 + 161.485872T - 31.38T\ln(T) + 1.616849 \times 10^{27}T^{-9}$	
	100–3000	$G(\mathrm{bct, Sn}) = +\mathrm{GHSER_{Sn}}$	[31]
		${}^{0}L^{\mathrm{bct}}_{\mathrm{Sb,Sn}} = +3659.1 - 21.3800T$	[26]
		${}^{1}L^{\mathrm{bct}}_{\mathrm{Sb,Sn}} = -21860.5 + 44.4870T$	[26]
		${}^{0}L^{\mathrm{bct}}_{\mathrm{Ge,Sb,Sn}} = +33324.0$	This work
		${}^{1}L^{\mathrm{bct}}_{\mathrm{Ge,Sb,Sn}} = +432242.3$	This work
		${}^{2}L^{\mathrm{bct}}_{\mathrm{Ge,Sb,Sn}} = +43230.0$	This work
SbSn		Model: $(\mathrm{Ge, Sb, Sn})_1(\mathrm{Ge, Sb,Sn})_1$	
		$G^{\mathrm{SbSn}}_{\mathrm{Sb:Sn}} = +\mathrm{GHSER_{Sb}} + \mathrm{GHSER_{Sn}} - 6035.7 - 2.4780T$	[26]
		$G^{\mathrm{SbSn}}_{\mathrm{Sn:Sb}} = +\mathrm{GHSER_{Sb}} + \mathrm{GHSER_{Sn}} - 6035.7 - 2.4780T$	[26]
		$G^{\mathrm{SbSn}}_{\mathrm{Sb:Sb}} = +2\mathrm{GHSER_{Sb}} + 6227.5$	[26]
		$G^{\mathrm{SbSn}}_{\mathrm{Sn:Sn}} = +2\mathrm{GHSER_{Sn}} + 7463.7$	[26]
		$G^{\mathrm{SbSn}}_{\mathrm{Ge:Ge}} = +2\mathrm{GHSER_{Ge}} + 11000.0$	This work
		$G^{\mathrm{SbSn}}_{\mathrm{Sn:Ge}} = +\mathrm{GHSER_{Sn}} + \mathrm{GHSER_{Ge}} + 51162.8$	This work
		$G^{\mathrm{SbSn}}_{\mathrm{Ge:Sn}} = +\mathrm{GHSER_{Sn}} + \mathrm{GHSER_{Ge}} + 51162.8$	This work
		$G^{\mathrm{SbSn}}_{\mathrm{Sb:Ge}} = +\mathrm{GHSER_{Sb}} + \mathrm{GHSER_{Ge}} + 53162.8$	This work
		$G^{\mathrm{SbSn}}_{\mathrm{Ge:Sb}} = +\mathrm{GHSER_{Sb}} + \mathrm{GHSER_{Ge}} + 53162.8$	This work
		${}^{0}L^{\mathrm{SbSn}}_{\mathrm{Sb,Sn:Sb}} = -4300.5 + 6.6380T$	[26]
		${}^{0}L^{\mathrm{SbSn}}_{\mathrm{Sb:Sb,Sn}} = -4300.5 + 6.6380T$	[26]
		${}^{0}L^{\mathrm{SbSn}}_{\mathrm{Sn:Sb,Sn}} = -1600.7 + 6.5990T$	[26]
		${}^{0}L^{\mathrm{SbSn}}_{\mathrm{Sb,Sb:Sn}} = -1600.7 + 6.5990T$	[26]
		${}^{0}L^{\mathrm{SbSn}}_{\mathrm{Sb:Ge,Sn}} = -15029.2$	This work
		${}^{0}L^{\mathrm{SbSn}}_{\mathrm{Ge,Sn:Sb}} = -15029.2$	This work
		${}^{0}L^{\mathrm{SbSn}}_{\mathrm{Sn:Ge,Sb}} = -15023.3$	This work
		${}^{0}L^{\mathrm{SbSn}}_{\mathrm{Ge,Sb:Sn}} = -15023.3$	This work
$\mathrm{Sb_2Sn_3}$		Model: $(\mathrm{Sb})_2(\mathrm{Sn})_3$	
		$G^{\mathrm{Sb_2Sn_3}}_{\mathrm{Sb:Sn}} = +2\mathrm{GHSER_{Sb}} + 3\mathrm{GHSER_{Sn}} - 232.6 - 31.0320T$	[26]

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

3.3. Intermetallic compounds

In the Ge–Sb–Sn system, the compound SbSn is treated as the formulae $(\mathrm{Ge,Sb,Sn})_1(\mathrm{Ge,Sb,Sn})_1$. The Gibbs energy per mole of formula unit SbSn is expressed as follows:

$$\begin{aligned}
G_{\mathrm{m}}^{\mathrm{SbSn}} = {} & y'_{\mathrm{Sb}}y''_{\mathrm{Ge}}G^{\mathrm{SbSn}}_{\mathrm{Sb:Ge}} + y'_{\mathrm{Sb}}y''_{\mathrm{Sb}}G^{\mathrm{SbSn}}_{\mathrm{Sb:Sb}} + y'_{\mathrm{Sb}}y''_{\mathrm{Sn}}G^{\mathrm{SbSn}}_{\mathrm{Sb:Sn}} + y'_{\mathrm{Sn}}y''_{\mathrm{Ge}}G^{\mathrm{SbSn}}_{\mathrm{Sn:Ge}} + y'_{\mathrm{Sn}}y''_{\mathrm{Sb}}G^{\mathrm{SbSn}}_{\mathrm{Sn:Sb}} + y'_{\mathrm{Sn}}y''_{\mathrm{Sn}}G^{\mathrm{SbSn}}_{\mathrm{Sn:Sn}} + y'_{\mathrm{Ge}}y''_{\mathrm{Sb}}G^{\mathrm{SbSn}}_{\mathrm{Ge:Sb}} + y'_{\mathrm{Ge}}y''_{\mathrm{Sn}}G^{\mathrm{SbSn}}_{\mathrm{Ge:Sn}} + y'_{\mathrm{Ge}}y''_{\mathrm{Ge}}G^{\mathrm{SbSn}}_{\mathrm{Ge:Ge}} \\
& + RT(y'_{\mathrm{Ge}}\ln y'_{\mathrm{Ge}} + y'_{\mathrm{Sb}}\ln y'_{\mathrm{Sb}} + y'_{\mathrm{Sn}}\ln y'_{\mathrm{Sn}}) + RT(y''_{\mathrm{Ge}}\ln y''_{\mathrm{Ge}} + y''_{\mathrm{Sb}}\ln y''_{\mathrm{Sb}} + y''_{\mathrm{Sn}}\ln y''_{\mathrm{Sn}}) \\
& + y'_{\mathrm{Ge}}\left[y''_{\mathrm{Ge}}y''_{\mathrm{Sb}}\sum_j {}^{j}L^{\mathrm{SbSn}}_{\mathrm{Ge:Ge,Sb}}(y''_{\mathrm{Ge}} - y''_{\mathrm{Sb}})^j + y''_{\mathrm{Ge}}y''_{\mathrm{Sn}}\sum_j {}^{j}L^{\mathrm{SbSn}}_{\mathrm{Ge:Ge,Sn}}(y''_{\mathrm{Ge}} - y''_{\mathrm{Sn}})^j + y''_{\mathrm{Sb}}y''_{\mathrm{Sn}}\sum_j {}^{j}L^{\mathrm{SbSn}}_{\mathrm{Ge:Sb,Sn}}(y''_{\mathrm{Sb}} - y''_{\mathrm{Sn}})^j + y''_{\mathrm{Ge}}y''_{\mathrm{Sb}}y''_{\mathrm{Sn}}\,{}^{j}L^{\mathrm{SbSn}}_{\mathrm{Ge:Ge,Sb,Sn}} \right] \\
& + y'_{\mathrm{Sb}}\left[y''_{\mathrm{Ge}}y''_{\mathrm{Sb}}\sum_j {}^{j}L^{\mathrm{SbSn}}_{\mathrm{Sb:Ge,Sb}}(y''_{\mathrm{Ge}} - y''_{\mathrm{Sb}})^j + y''_{\mathrm{Ge}}y''_{\mathrm{Sn}}\sum_j {}^{j}L^{\mathrm{SbSn}}_{\mathrm{Sb:Ge,Sn}}(y''_{\mathrm{Ge}} - y''_{\mathrm{Sn}})^j + y''_{\mathrm{Sb}}y''_{\mathrm{Sn}}\sum_j {}^{j}L^{\mathrm{SbSn}}_{\mathrm{Sb:Sb,Sn}}(y''_{\mathrm{Sb}} - y''_{\mathrm{Sn}})^j + y''_{\mathrm{Ge}}y''_{\mathrm{Sb}}y''_{\mathrm{Sn}}\,{}^{j}L^{\mathrm{SbSn}}_{\mathrm{Sb:Ge,Sb,Sn}} \right] \\
& + y'_{\mathrm{Sn}}\left[y''_{\mathrm{Ge}}y''_{\mathrm{Sb}}\sum_j {}^{j}L^{\mathrm{SbSn}}_{\mathrm{Sn:Ge,Sb}}(y''_{\mathrm{Ge}} - y''_{\mathrm{Sb}})^j + y''_{\mathrm{Ge}}y''_{\mathrm{Sn}}\sum_j {}^{j}L^{\mathrm{SbSn}}_{\mathrm{Sn:Ge,Sn}}(y''_{\mathrm{Ge}} - y''_{\mathrm{Sn}})^j + y''_{\mathrm{Sb}}y''_{\mathrm{Sn}}\sum_j {}^{j}L^{\mathrm{SbSn}}_{\mathrm{Sn:Sb,Sn}}(y''_{\mathrm{Sb}} - y''_{\mathrm{Sn}})^j + y''_{\mathrm{Ge}}y''_{\mathrm{Sb}}y''_{\mathrm{Sn}}\,{}^{j}L^{\mathrm{SbSn}}_{\mathrm{Sn:Ge,Sb,Sn}} \right] \quad (7) \\
& + y''_{\mathrm{Ge}}\left[y'_{\mathrm{Ge}}y'_{\mathrm{Sb}}\sum_j {}^{j}L^{\mathrm{SbSn}}_{\mathrm{Ge,Sb:Ge}}(y'_{\mathrm{Ge}} - y'_{\mathrm{Sb}})^j + y'_{\mathrm{Ge}}y'_{\mathrm{Sn}}\sum_j {}^{j}L^{\mathrm{SbSn}}_{\mathrm{Ge,Sn:Ge}}(y'_{\mathrm{Ge}} - y'_{\mathrm{Sn}})^j + y'_{\mathrm{Sb}}y'_{\mathrm{Sn}}\sum_j {}^{j}L^{\mathrm{SbSn}}_{\mathrm{Sb,Sn:Ge}}(y'_{\mathrm{Sb}} - y'_{\mathrm{Sn}})^j + y'_{\mathrm{Ge}}y'_{\mathrm{Sb}}y'_{\mathrm{Sn}}\,{}^{j}L^{\mathrm{SbSn}}_{\mathrm{Ge,Sb,Sn:Ge}} \right] \\
& + y''_{\mathrm{Sb}}\left[y'_{\mathrm{Ge}}y'_{\mathrm{Sb}}\sum_j {}^{j}L^{\mathrm{SbSn}}_{\mathrm{Ge,Sb:Sb}}(y'_{\mathrm{Ge}} - y'_{\mathrm{Sb}})^j + y'_{\mathrm{Ge}}y'_{\mathrm{Sn}}\sum_j {}^{j}L^{\mathrm{SbSn}}_{\mathrm{Ge,Sn:Sb}}(y'_{\mathrm{Ge}} - y'_{\mathrm{Sn}})^j + y'_{\mathrm{Sb}}y'_{\mathrm{Sn}}\sum_j {}^{j}L^{\mathrm{SbSn}}_{\mathrm{Sb,Sn:Sb}}(y'_{\mathrm{Sb}} - y'_{\mathrm{Sn}})^j + y'_{\mathrm{Ge}}y'_{\mathrm{Sb}}y'_{\mathrm{Sn}}\,{}^{j}L^{\mathrm{SbSn}}_{\mathrm{Ge,Sb,Sn:Sb}} \right] \\
& + y''_{\mathrm{Sn}}\left[y'_{\mathrm{Ge}}y'_{\mathrm{Sb}}\sum_j {}^{j}L^{\mathrm{SbSn}}_{\mathrm{Ge,Sb:Sn}}(y'_{\mathrm{Ge}} - y'_{\mathrm{Sb}})^j + y'_{\mathrm{Ge}}y'_{\mathrm{Sn}}\sum_j {}^{j}L^{\mathrm{SbSn}}_{\mathrm{Ge,Sn:Sn}}(y'_{\mathrm{Ge}} - y'_{\mathrm{Sn}})^j + y'_{\mathrm{Sb}}y'_{\mathrm{Sn}}\sum_j {}^{j}L^{\mathrm{SbSn}}_{\mathrm{Sb,Sn:Sn}}(y'_{\mathrm{Sb}} - y'_{\mathrm{Sn}})^j + y'_{\mathrm{Ge}}y'_{\mathrm{Sb}}y'_{\mathrm{Sn}}\,{}^{j}L^{\mathrm{SbSn}}_{\mathrm{Ge,Sb,Sn:Sn}} \right]
\end{aligned}$$

where y'_* and y''_* are the site fraction of Ge, Sb or Sn on the first and second sublattices, respectively; the parameter $G^{\mathrm{SbSn}}_{*:*}$ represents the Gibbs energies of the compound SbSn when the first and second sublattices are occupied by only one element Ge, Sb or Sn, respectively, which are relative to the enthalpies of diamond for Ge, rhom for Sb, and bct for Sn in their SER state; ${}^{j}L^{\mathrm{SbSn}}_{\mathrm{Ge,Sb:*}}$, ${}^{j}L^{\mathrm{SbSn}}_{\mathrm{Ge,Sn:*}}$, ${}^{j}L^{\mathrm{SbSn}}_{\mathrm{Sb,Sn:*}}$, ${}^{j}L^{\mathrm{SbSn}}_{\mathrm{*:Ge,Sb}}$, ${}^{j}L^{\mathrm{SbSn}}_{\mathrm{*:Ge,Sn}}$ and ${}^{j}L^{\mathrm{SbSn}}_{\mathrm{*:Sb,Sn}}$ are the jth interaction parameter between elements Ge and Sb, Ge and Sn, and Sb and Sn on the first and second sublattice, respectively; ${}^{j}L^{\mathrm{SbSn}}_{\mathrm{Ge,Sb,Sn:*}}$ and ${}^{j}L^{\mathrm{SbSn}}_{\mathrm{*:Ge,Sb,Sn}}$ represents the jth interaction parameter among elements Ge, Sb and Sn on the first and second sublattice, respectively.

In the ternary Ge–Sb–Sn system, the solid solubility of Ge in the binary compound $\mathrm{Sb_2Sn_3}$ is very small and closed to 0. In the present work, the model of $\mathrm{Sb_2Sn_3}$ is consistent with that in the Sb–Sn system [26]. The Gibbs energy per mole of formula unit $\mathrm{Sb_2Sn_3}$ is expressed as following:

$$G_{\mathrm{m}}^{\mathrm{Sb_2Sn_3}} = 2\mathrm{GHSER_{Sb}} + 3\mathrm{GHSER_{Sn}} + \Delta G_{\mathrm{f}}^{\mathrm{Sb_2Sn_3}} \quad (8)$$

where $\Delta G_{\mathrm{f}}^{\mathrm{Sb_2Sn_3}}$ is the Gibbs energy of formation per mole of formula unit $\mathrm{Sb_2Sn_3}$. Owing to a lack of experimental measurements, it is assumed that the Neumann–Kopp rule applies to the heat capacity, i.e. $\Delta C_P = 0$. Thus, $\Delta G_{\mathrm{f}}^{\mathrm{Sb_2Sn_3}}$ can be given by the following expression:

$$\Delta G_{\mathrm{f}}^{\mathrm{Sb_2Sn_3}} = a + bT \quad (9)$$

where the parameters a and b were taken from the assessed results in Ref. [26].

3.4. Assessment procedure

A general rule for selection of the adjustable parameters is that only those coefficients determined by the experimental values should be adjusted [33]. The assessment is carried out by means of the optimization module PARROT of the thermodynamic software Thermo-Calc [34], which can deal with various kinds of experimental information.

A careful examination of thermodynamic descriptions of the Ge–Sn [22] and the Sb–Sn [26] systems is made. The thermodynamic optimization of the Ge–Sb and the Ge–Sb–Sn systems were carefully performed in this work.

The thermodynamic parameters for the Ge–Sb system are re-optimized on the basis of the information [5–20]. The experimental results reported by Nasir et al. [20] are given more weight during the optimizing procedure. For liquid and rhom, the interaction parameters ${}^{0}L^{\mathrm{liq.}}_{\mathrm{Ge,Sb}}$, ${}^{1}L^{\mathrm{liq.}}_{\mathrm{Ge,Sb}}$ and ${}^{0}L^{\mathrm{rhom}}_{\mathrm{Ge,Sb}}$ in Eq. (5) can be reliably obtained from the experimental data. The interaction parameter ${}^{0}L^{\mathrm{diamond}}_{\mathrm{Ge,Sb}}$ is taken from the assessed data [19].

The thermodynamic parameters for the Ge–Sb–Sn system are optimized on the basis of the experimental information available in the literature [28,30]. The experimental results reported by Dichi et al. [30] are given more weight during the process of optimization.

The thermodynamic parameters of liquid, diamond, rhom and bct in the Ge–Sb–Sn system, are obtained by a combination of the corresponding Gibbs energy functions from the assessments of the binary systems using Muggianu interpolation of binary excess terms [35]. The interaction parameters ${}^{0}L^{\mathrm{liq.}}_{\mathrm{Ge,Sn}}$, ${}^{1}L^{\mathrm{liq.}}_{\mathrm{Ge,Sn}}$, ${}^{0}L^{\mathrm{liq.}}_{\mathrm{Sb,Sn}}$, ${}^{1}L^{\mathrm{liq.}}_{\mathrm{Sb,Sn}}$, ${}^{2}L^{\mathrm{liq.}}_{\mathrm{Sb,Sn}}$, ${}^{0}L^{\mathrm{rhom}}_{\mathrm{Sb,Sn}}$, ${}^{0}L^{\mathrm{bct}}_{\mathrm{Sb,Sn}}$ and ${}^{1}L^{\mathrm{bct}}_{\mathrm{Sb,Sn}}$ are taken from the two binary systems assessed by Feutelais et al. [22] and Kroupa and Vízdal [26]. The ternary parameters ${}^{0}L^{\mathrm{liq}}_{\mathrm{Ge,Sb,Sn}}$, ${}^{1}L^{\mathrm{liq}}_{\mathrm{Ge,Sb,Sn}}$, ${}^{2}L^{\mathrm{liq}}_{\mathrm{Ge,Sb,Sn}}$, ${}^{0}L^{\mathrm{rhom}}_{\mathrm{Ge,Sb,Sn}}$, ${}^{1}L^{\mathrm{rhom}}_{\mathrm{Ge,Sb,Sn}}$, ${}^{2}L^{\mathrm{rhom}}_{\mathrm{Ge,Sb,Sn}}$, ${}^{0}L^{\mathrm{bct}}_{\mathrm{Ge,Sb,Sn}}$, ${}^{1}L^{\mathrm{bct}}_{\mathrm{Ge,Sb,Sn}}$ and ${}^{2}L^{\mathrm{bct}}_{\mathrm{Ge,Sb,Sn}}$ are optimized according to the experimental data [28,30].

For the compounds in the ternary Ge–Sb–Sn system, the parameters $G^{\mathrm{SbSn}}_{\mathrm{Sb:Sn}}$, $G^{\mathrm{SbSn}}_{\mathrm{Sb:Sb}}$, $G^{\mathrm{SbSn}}_{\mathrm{Sn:Sn}}$, $G^{\mathrm{SbSn}}_{\mathrm{Sn:Sb}}$, $G^{\mathrm{Sb_2Sn_3}}_{\mathrm{Sb:Sn}}$, ${}^{0}L^{\mathrm{SbSn}}_{\mathrm{Sb,Sn:Sb}}$, ${}^{0}L^{\mathrm{SbSn}}_{\mathrm{Sb:Sn,Sb}}$, ${}^{0}L^{\mathrm{SbSn}}_{\mathrm{Sn:Sn,Sb}}$ and ${}^{0}L^{\mathrm{SbSn}}_{\mathrm{Sb,Sn:Sn}}$ are taken from the thermodynamic description of the binary Sb–Sn system. The parameters $G^{\mathrm{SbSn}}_{\mathrm{Ge:Sb}}$, $G^{\mathrm{SbSn}}_{\mathrm{Sb:Ge}}$ $G^{\mathrm{SbSn}}_{\mathrm{Ge:Sn}}$, $G^{\mathrm{SbSn}}_{\mathrm{Sn:Ge}}$, $G^{\mathrm{SbSn}}_{\mathrm{Ge:Ge}}$, ${}^{0}L^{\mathrm{SbSn}}_{\mathrm{Sb:Ge,Sn}}$, ${}^{0}L^{\mathrm{SbSn}}_{\mathrm{Sn:Ge,Sb}}$, ${}^{0}L^{\mathrm{SbSn}}_{\mathrm{Ge,Sn:Sb}}$ and ${}^{0}L^{\mathrm{SbSn}}_{\mathrm{Ge,Sb:Sn}}$ are optimized according to the experimental data [30]. For the reason of crystallographic symmetry, the number of the parameters is reduced by the following assumption:

$$G^{\mathrm{SbSn}}_{\mathrm{Ge:Sb}} = G^{\mathrm{SbSn}}_{\mathrm{Sb:Ge}} \quad (10)$$

$$G^{\mathrm{SbSn}}_{\mathrm{Ge:Sn}} = G^{\mathrm{SbSn}}_{\mathrm{Sn:Ge}} \quad (11)$$

$${}^{0}L^{\mathrm{SbSn}}_{\mathrm{Sb:Ge,Sn}} = {}^{0}L^{\mathrm{SbSn}}_{\mathrm{Ge,Sn:Sb}} \quad (12)$$

$${}^{0}L^{\mathrm{SbSn}}_{\mathrm{Sn:Ge,Sb}} = {}^{0}L^{\mathrm{SbSn}}_{\mathrm{Ge,Sb:Sn}} \quad (13)$$

Table 2
Invariant reactions of the Ge–Sb system.

Reaction	Present work				Experimental data				
	T (K)	x(Sb)			T (K)	x(Sb)			Ref.
Liq. → diamond + rhom	865	0.8249	0.0001	0.9375	859	0.832	–	–	[5]
					865	0.865	0.000	1.000	[6]
					865	0.855	0.000	1.000	[14]
					859	0.838	0.000	1.000	[15]
					860	0.857	0.0001	1.000	[19]
					865	0.775	0.000	0.937	[20]

Table 3
Invariant reactions of the Ge–Sb–Sn system.

Reaction	Present work					Ref. [30]
	Type	T (K)	Composition in liquid			T (K)
			x(Ge)	x(Sb)	x(Sn)	
Liq. + rhom → SbSn + diamond	U_1	692	0.0219	0.4898	0.4883	692
Liq. + SbSn → Sb_2Sn_3 + diamond	U_2	594	0.0057	0.2054	0.7889	594
Liq. + Sb_2Sn_3 → bct + diamond	U_3	518	0.0821	0.0089	0.9090	518
Sb_2Sn_3 → bct + diamond + SbSn	E	516	–	–	–	516

4. Results and calculations

4.1. The Ge–Sn and Sb–Sn systems

The Ge–Sn and Sb–Sn systems were assessed by Feutelais et al. [22] and Kroupa and Vízdal [26], respectively. Their thermodynamic descriptions are accepted in the present work and listed in Table 1.

4.2. The Ge–Sb system

The calculated Ge–Sb phase diagram using the thermodynamic parameters optimized in this work and comparison with the experimental data [5–9,20] is shown in Fig. 3.

Fig. 4 presents the calculated enthalpy of mixing of liquid at 1273 K in comparison with experimental data [17,18]. The experimental results reported by Predel and Stein [17] and Alfer et al. [18] are given the same weight during the optimizing procedure. To well reproduce the activities of Ge and Sb in liquid reported by Kostov et al. [16], the calculated results are in agreement with the experimental data [17], as shown in Fig. 4.

The calculated activities of Ge and Sb in liquid at 1073, 1173 and 1273 K in comparison with the measured data [16] are shown in Fig. 5a–c. Satisfactory agreement is obtained between the calculated results and the experimental data [16]. The thermodynamic parameters of the Ge–Sb system obtained in the present work are listed in Table 1. The calculated invariant reaction in the Ge–Sb system is listed in Table 2. The experimental invariant reaction temperature and compositions of individual phases [20] are well reproduced.

4.3. The Ge–Sb–Sn system

Combining the Ge–Sb system assessed in the present work with the Ge–Sn [22] and Sb–Sn [26] systems optimized previously, the Ge–Sb–Sn system has been optimized on the basis of the available experimental information [28,30].

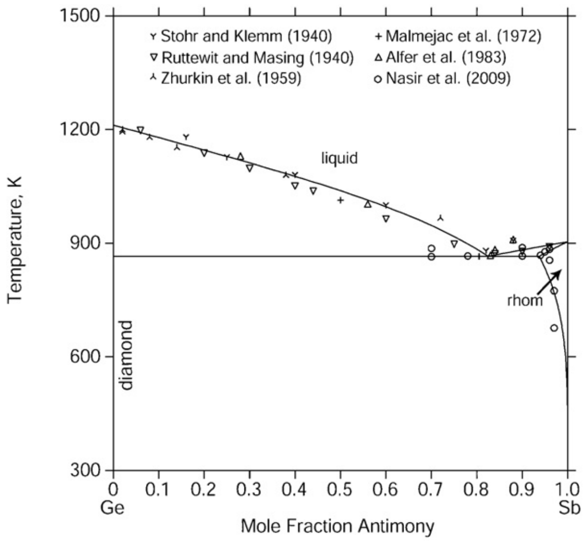

Fig. 3. Calculated Ge–Sb phase diagram by the present thermodynamic description with experimental data measured by Stöhr and Klemm [5], Ruttewit and Masing [6], Zhurkin et al. [7], Malmejac et al. [8], Alfer et al. [9] and Nasir et al. [20].

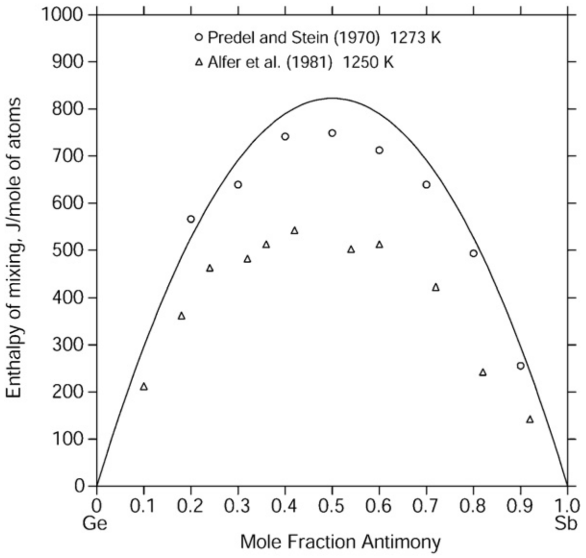

Fig. 4. Calculated enthalpies of mixing of liquid at 1273 K in the Ge–Sb system and comparison with the experimental data [17,18]. The reference states are liquid for Ge and Sb.

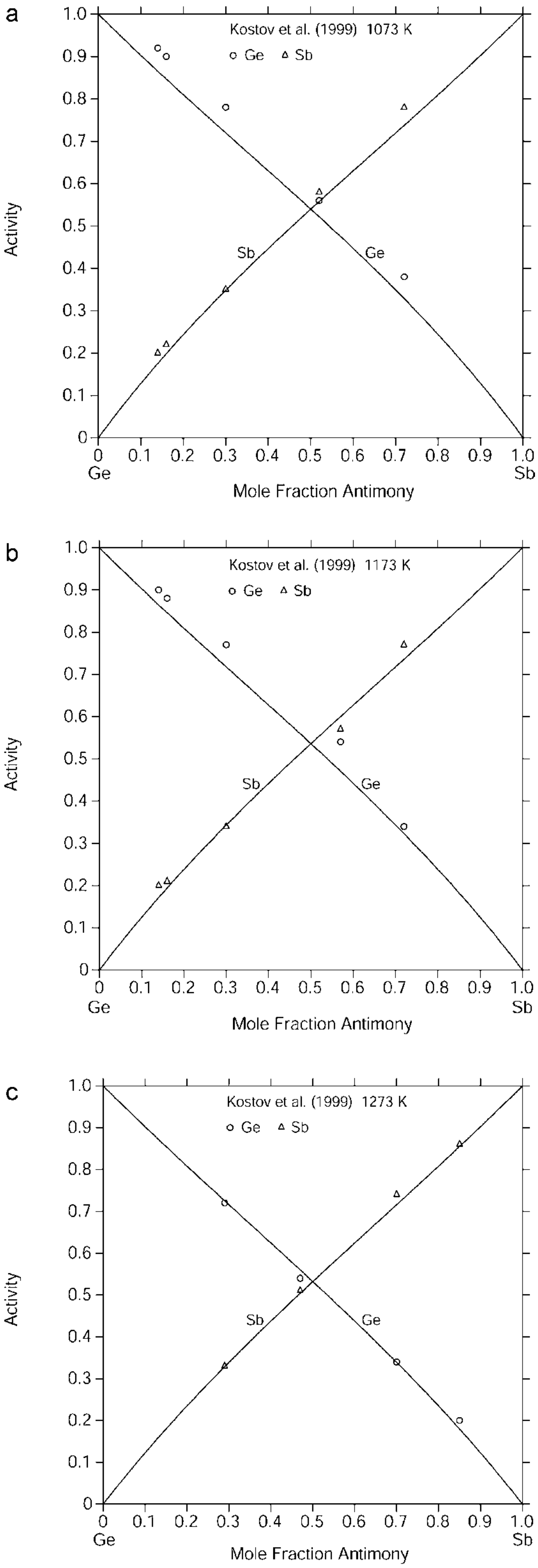

Fig. 5. (a) Calculated activities of Ge and Sb in liquid at 1073 K in the Ge–Sb system and comparison with the experimental data [16]. The reference states are liquid for Ge and Sb. (b) Calculated activities of Ge and Sb in liquid at 1173 K in the Ge–Sb system and comparison with the experimental data [16]. The reference states are liquid for Ge and Sb. (c) Calculated activities of Ge and Sb in liquid at 1273 K in the Ge–Sb system and comparison with the experimental data [16]. The reference states are liquid for Ge and Sb.

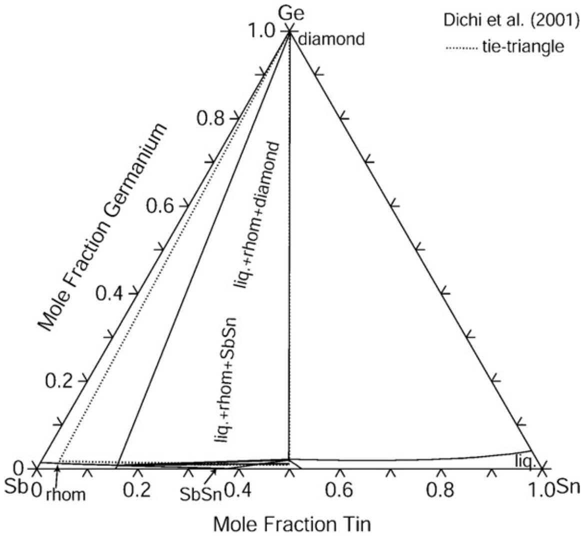

Fig. 6. Calculated isothermal section of the Ge–Sb–Sn system at 692 K by the present thermodynamic description and comparison with the experimental data [30].

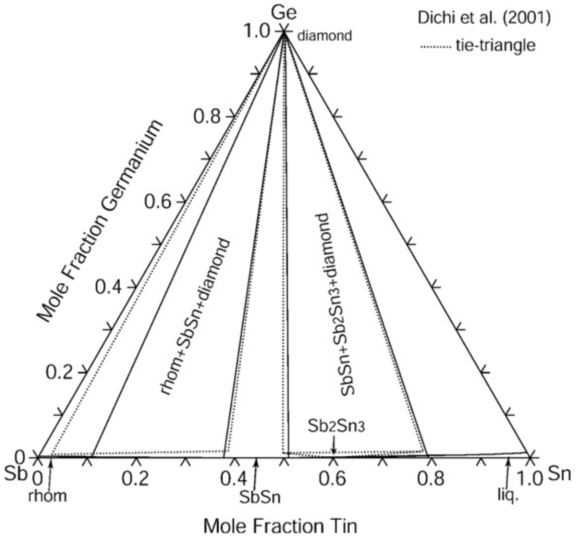

Fig. 7. Calculated isothermal section of the Ge–Sb–Sn system at 594 K by the present thermodynamic description and comparison with the experimental data [30].

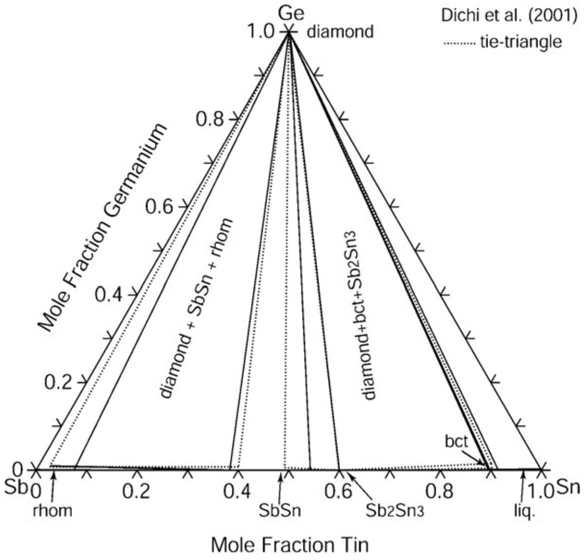

Fig. 8. Calculated isothermal section of the Ge–Sb–Sn system at 518 K by the present thermodynamic description and comparison with the experimental data [30].

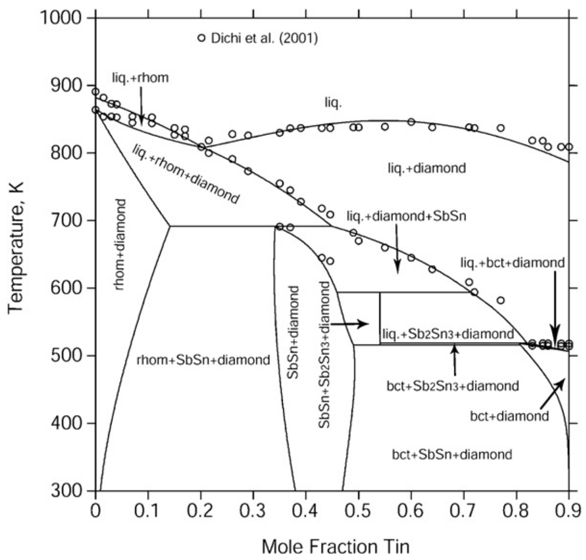

Fig. 9. Calculated vertical section of the Ge–Sb–Sn system at 10 at.% Ge by the present description and comparison with the experimental data [30].

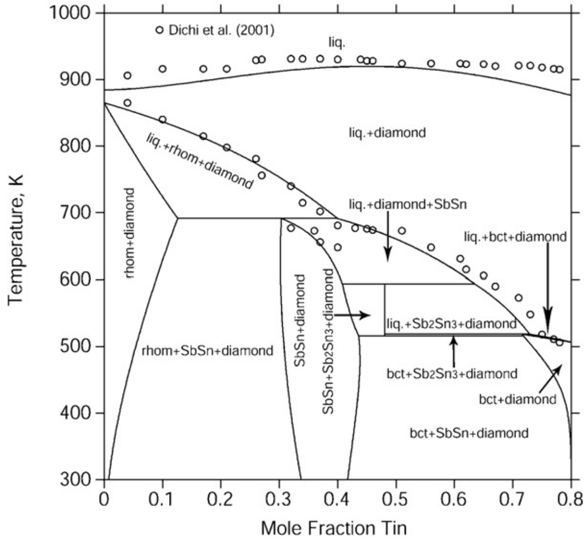

Fig. 10. Calculated vertical section of the Ge–Sb–Sn system at 20 at.% Ge by the present description and comparison with the experimental data [30].

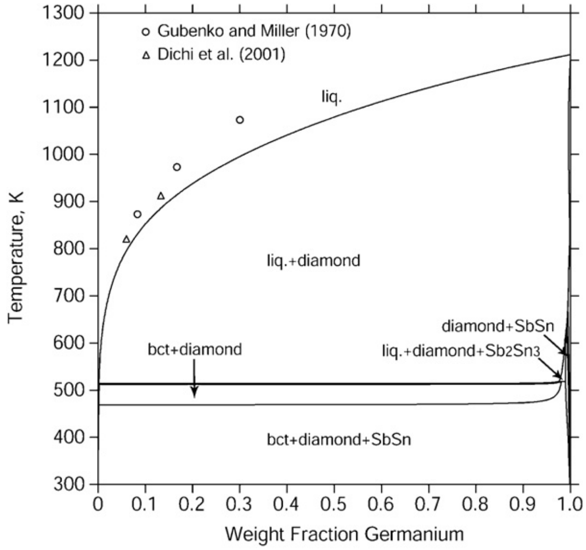

Fig. 11. Calculated vertical section of the Ge–Sb–Sn system at Ge–(Sn + 5.5 wt.% Sb) by the present description and comparison with the experimental data [28,30].

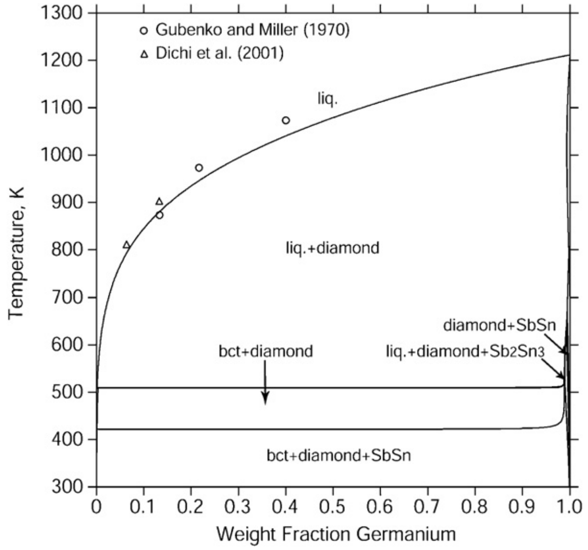

Fig. 12. Calculated vertical section of the Ge–Sb–Sn system at Ge–(Sn + 2 wt.%Sb) by the present description and comparison with the experimental data [28,30].

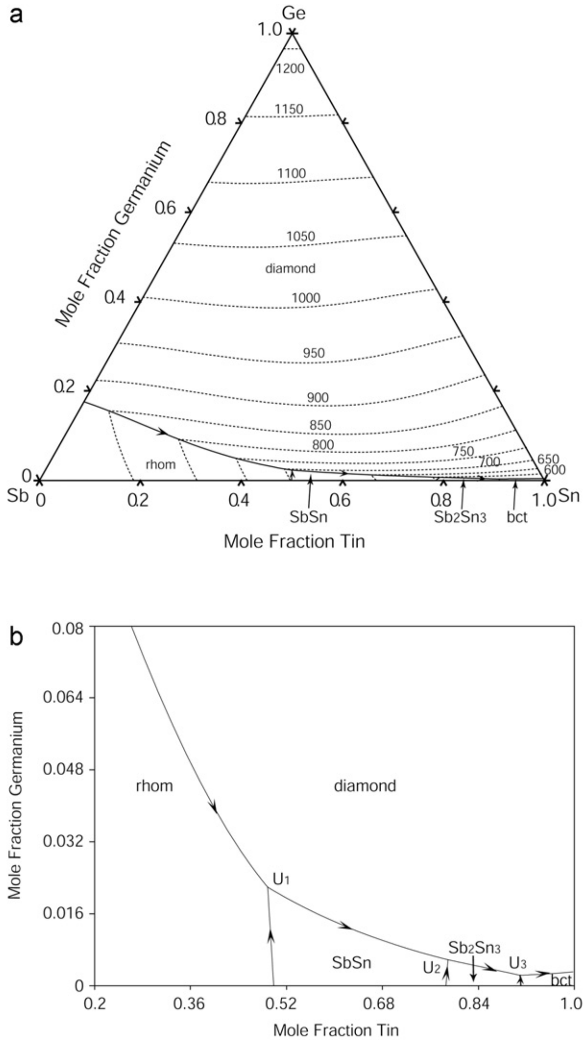

Fig. 13. (a) Calculated projection of the liquidus surfaces in the Ge–Sb–Sn system using the present thermodynamic description. (b) Enlarged section of (a).

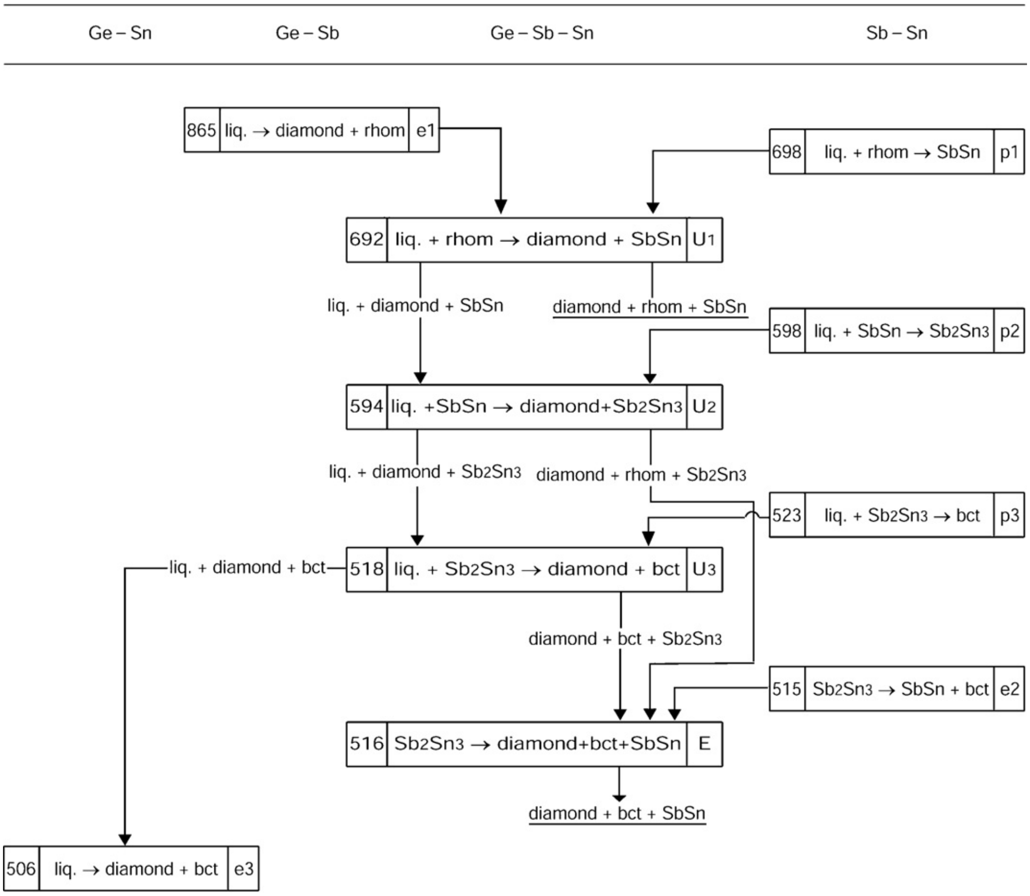

Fig. 14. Calculated complete reaction scheme of the Ge–Sb–Sn system.

The thermodynamic description of the Ge–Sb–Sn system obtained in the present work is shown in Table 1.

The calculated invariant equilibria in the Ge–Sb–Sn system are listed in Table 3. As shown in the table, a very good agreement is obtained between the calculated results and the experimental data [30].

Figs. 6–8 are the calculated isothermal sections at 692, 594 and 518 K in the Ge–Sb–Sn system, respectively. Figs. 9 and 10 are the calculated vertical sections at 10 and 20 at.% Ge using the present thermodynamic description in comparison with experimental data [30] in the Ge–Sb–Sn system. Satisfactory agreements are obtained between the calculated results and the experimental data [30] in Figs. 6–9. The discrepancy in liquidus in Fig. 10 between the calculated results and experimental data [30] was caused by the optimized results in the binary Ge–Sb and Ge–Sn [22] systems.

Figs. 11 and 12 are the calculated vertical sections at Ge–(Sn + 5.5 wt. % Sb) and Ge–(Sn + 2 wt. % Sb) using the present thermodynamic description in the Ge–Sb–Sn system with experimental data [28,30]. The experimental results reported by Dichi et al. [30] are given more weight during the optimizing procedure. The calculated results are some deviations with experiments [28], but satisfactory agreement is obtained between the calculations and the experiments [30].

Fig. 13a and b is the calculated projection of the liquidus surfaces of the Ge–Sb–Sn system according by the present thermodynamic description. Fig. 14 shows the predicted entire reaction scheme for the Ge–Sb–Sn system. The calculated projection of liquidus surfaces and the reaction scheme in the Ge–Sb–Sn system are consistent with the experimental results [30].

5. Conclusions

The thermodynamic parameters in the Ge–Sb binary system and the Ge–Sb–Sn ternary system are critically evaluated from the experimental information available in the literature. A set of self-consistent thermodynamic parameters describing the Gibbs energy of each individual phase as a function of composition and temperature is derived. The projection of the liquidus surfaces and the entire reaction scheme for the Ge–Sb–Sn system are well reproduced.

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