

Thermodynamic Description of the Quaternary Ag-Bi-Cu-Sn System

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Lead-free soldering is an important part of electronic devices production. New lead-free solders that replace classical Sn-37Pb solder are still under development. Thermodynamic modeling makes the development process faster, cheaper and more environmentally friendly due to predictions of phases stabilities and phases transformations. In this work, the thermodynamic description of quaternary Ag-Bi-Cu-Sn system is presented. The thermodynamic assessment of promising lead-free quaternary solder was prepared using the Calphad approach. A good agreement between available experimental data and calculation was found.

Key words: Lead-free solder, Calphad, thermodynamics

INTRODUCTION

Lead-free solders play important roles in the electronic industry. They have been studied for several years and their thermodynamic descriptions can be found in the literature. However; thermodynamic reports about quaternary systems are rare, and there is still a lack of information about their thermodynamics. The quaternary Ag-Bi-Cu-Sn alloy has been used as a lead-free solder,¹ and therefore knowledge about its phase equilibria and phase transformations is crucial for industrial applications. Moreover, the quaternary equilibria can explain the reactions between Cu-substrates and Ag-Bi-Sn solders.² Furthermore, the CALPHAD³ method used in this work allows for quite easy extension of the quaternary system to higher-ordered systems.

LITERATURE REVIEW

The quaternary Ag-Bi-Cu-Sn system includes four ternaries: Ag-Bi-Cu, Ag-Bi-Sn, Ag-Cu-Sn and Bi-Cu-Sn. Detailed information about the ternary Ag-Cu-Sn system was published by the author in his previous work on this system.⁴ The ternary Ag-Bi-Sn was described by Chen et al.⁵ Bearing in mind

that one of the goals of this work is to keep the thermodynamic description of Ag-Bi-Cu-Sn system consistent with previous works carried out by the author, thermodynamic descriptions of binaries Ag-Cu, Ag-Sn, Ag-Bi, Cu-Sn and Bi-Sn were taken from previous assessments.^{4,5} The thermodynamic description of binary Cu-Bi given in COST531⁶ database was applied in this work.

The ternary Bi-Cu-Sn system has been investigated by several researchers. Yen et al.⁷ determined the isothermal section at 673 K and at 393 K using standard phase equilibrium determination techniques. Yen et al.⁷ found that the solubility of Bi in intermetallic compounds (IMCs) Cu₆Sn₅ and Cu₃Sn is negligible and does not exceed 0.5 at.%. The same system was investigated by Doi et al.⁸ who examined isoplethal sections for different amounts of Sn (10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, and 90%) using the differential scanning calorimetry (DSC) method. It is interesting that Doi et al.⁸ found a miscibility gap in the liquid phase, what is opposite to the liquidus projection provided by the National Institute of Standards and Technology (NIST).⁹ Thermodynamic properties of the Bi-Cu-Sn system were investigated by Kopyto et al.¹⁰ who determined the activity of tin in the liquid phase using electromotive force measurement (EMF). Kopyto et al.¹⁰ examined EMF for three intersections of $x_{\text{Bi}}/x_{\text{Cu}}$: 3, 1 and 1/3, in the temperature range

973–1325 K. The measured activity of tin shows a negative deviation from Raoult's Law for all three sections at 1273 K and an S-shape for 1073 K, with negative deviation for a concentration of Sn smaller than 0.6 mol fraction and positive deviation for Sn concentration higher than 0.6 mol fraction. Romanowska¹¹ investigated the activity of Bi in the liquid alloys Bi-Cu-Sn using vapor saturation method at 1373 K, 1423 K, and 1473 K. According to Romanowska's¹¹ results, the activity of Bismuth shows a positive deviation from Raoult's Law for all concentrations at the temperatures of measurement. The enthalpy of mixing of a liquid Bi-Cu-Sn system was measured by Flandorfer et al.¹² using the drop calorimetry method for 9 intersections at 1023 K. The excess enthalpy reported by Flandorfer et al.¹² shows positive values for the majority of compositions, except the Cu-Sn side, due to strong, negative values of liquid mixing enthalpy in the binary Cu-Sn liquid. To the best of the author's knowledge, there is no published critical assessment of the ternary Bi-Cu-Sn system; however, it should be mentioned that Doi et al.⁸ provided a calculated liquidus projection of the Bi-Cu-Sn system, and proposed interaction parameters for the liquid phase $L_{\text{Bi,Cu,Sn}}^{0,1,2} = 10,000$.

The Ag-Bi-Cu alloy is a simple ternary system made of three binary eutectic systems. Literature information about Ag-Bi-Cu is very limited. Fima and Garzel¹³ analyzed the microstructure of as-cast alloys for 3 intersections, $x_{\text{Ag}}/x_{\text{Bi}}$: 4, 1, and $\frac{1}{4}$. They found that there is virtually no mutual solubility of all the components. Moreover, they performed differential thermal analysis (DTA) of all 24 alloys. Thermodynamic properties of liquid were measured by Fima and Flandorfer¹⁴ who investigated the enthalpy of mixing at 1073 K for six different intersections. All heat effects reported by Fima and Flandorfer¹⁴ exhibited positive values.

The quaternary system Ag-Bi-Cu-Sn was examined by Doi et al.⁸ who used DSC measurements to establish an isoplethal section Sn-Bi-2 wt.% Ag-0.7 wt.% Cu. Thermodynamic properties of liquid Ag-Bi-Cu-Sn were determined by Garzel et al.¹⁵ who utilized EMF measurements of Sn activity in the temperature range 950–1300 K for four intersections: $x_{\text{Ag}}:x_{\text{Bi}}:x_{\text{Cu}} = 1$, $x_{\text{Ag}}/(x_{\text{Bi}} + x_{\text{Cu}}) = 3/2$ for $x_{\text{Bi}} = x_{\text{Cu}}$, $x_{\text{Bi}}/(x_{\text{Ag}} + x_{\text{Cu}}) = 3/2$ for $x_{\text{Ag}} = x_{\text{Cu}}$, and $x_{\text{Cu}}/(x_{\text{Ag}} + x_{\text{Bi}}) = 3/2$ for $x_{\text{Ag}} = x_{\text{Bi}}$. The measured activity of Sn shows a slightly negative deviation from Raoult's Law for all intersections, except intersection $x_{\text{Bi}}/(x_{\text{Ag}} + x_{\text{Cu}}) = 3/2$, where Sn activity shows a big positive deviation for the concentration around 0.6 mol fraction. Garzel et al.¹⁵ explained this behavior by assuming a miscibility gap in the liquid phase around this particular concentration. Wu et al.¹⁶ proposed a development of a lead-free solder, Sn-6 wt.% Bi-2 wt.% Ag-0.5 wt.% Cu, by mechanical alloying. According to

their results, the proposed solder shows a melting temperature at a range 467.02–483.03 K (193.87–209.88°C) and presents much better mechanical properties than either classical Sn-37Pb solder or Sn-3.5Ag lead-free solder. The quaternary Ag-Bi-Cu-Sn system includes 11 phases. Information about their crystal structures is gathered in Table I.¹⁷

THERMODYNAMIC MODELS

The following phases are considered in this work: FCC_A1, BCT_A5, rhombohedral_A7, BCC_A2, HCP_A3, Liquid, $\text{Cu}_{41}\text{Sn}_{11}$, $\text{Cu}_{10}\text{Sn}_3$, Cu_3Sn , Cu_6Sn_5 , and AGSB_ORTHO. Detailed information about these phases is given in Table I¹⁷ and below.

Substitutional Solution: FCC_A1, BCC_A2, BCT_A5, Liquid

The Gibbs free energies of pure elements with respect to temperature ${}^0G_i(T) = G_i(T) - H_i^{\text{SER}}$ are represented by Eq. 1:

$${}^0G_i(T) = a + bT + cT \ln(T) + dT^2 + eT^{-1} + fT^3 + iT^4 + jT^7 + kT^{-9} \quad (1)$$

The ${}^0G_i(T)$ data are referred to the constant enthalpy value of the standard element reference $H_i(T)$ at 298.15 K and 1 bar as recommended by the Scientific Group Thermodata Europe (SGTE).¹⁸ The reference states are: FCC_A1 (Cu and Ag), BCT_A5 (Sn), and rhombohedral_A7(Bi). The ${}^0G_i(T)$ expression may be given for several temperature ranges, where the coefficients $a, b, c, d, e, f, i, j, k$ have different values. The ${}^0G_i(T)$ functions are taken from SGTE Unary (pure elements) thermodynamic database (TDB) v.5.¹⁸ Solid and liquid solution phases (FCC_A1, BCC_A2, BCT_A5, HCP_A3, and liquid) are described by the substitutional solution model¹⁹:

Table I. Crystal structures of phases in quaternary Ag-Bi-Cu-Sn system¹⁷

Phase	Pearson symbol	Space group
FCC_A1	cF4	Fm $\bar{3}$ m
RHOMBOHEDRAL_A7	hR2	R $\bar{3}$ m
HCP_A3	hP2	P6 ₃ /mmc
AGSB_ORTHO	oP8	Pmmn
BCC_A2	cI2	Im $\bar{3}$ m
CU41SN11	hP26	P6 ₃
CU6SN5	hP4	P6 ₃ /mmc
CU10SN3	cF416	F43m
CU3SN	oC80	Cmcm
BCT_A5	tI4	I4 ₁ /amd

Table II. Gibbs energies and interaction parameters of phases in the Ag-Bi-Cu-Sn system

Phase	Function	Reference	
BCC_A2	${}^0L_{Ag,Cu:Va}^{BCC_A2} = 36,772.58 - 11.02847 \times T$	Ref. 4	
	${}^1L_{Ag,Cu:Va}^{BCC_A2} = -4612.43 + 0.28869 \times T$	Ref. 4	
	${}^0L_{Ag,Bi:Va}^{BCC_A2} = 250 - 77.78 - 12.05475 \times T$	Ref. 5	
	${}^0L_{Ag,Sn:Va}^{BCC_A2} = 7000$	Ref. 4	
	${}^0L_{Cu,Sn:Va}^{BCC_A2} = 5497.236 - 22.307629 \times T$	Ref. 4	
	${}^1L_{Cu,Sn:Va}^{BCC_A2} = -77,713.554 + 60.253852 \times T$	Ref. 4	
	${}^2L_{Cu,Sn:Va}^{BCC_A2} = -1.73319 - 19.2002 \times T$	Ref. 4	
	${}^0L_{Ag,Cu,Sn:Va}^{BCC_A2} = -95,000$	Ref. 4	
	${}^1L_{Ag,Cu,Sn:Va}^{BCC_A2} = -24,2000 - 8 \times T$	Ref. 4	
	${}^2L_{Ag,Cu,Sn:Va}^{BCC_A2} = +95,000$	Ref. 4	
	BCT_A5	${}^0L_{Ag,Bi}^{BCT_A5} = 25,077.78 - 12.05475 \times T$	Ref. 5
		${}^0L_{Ag,Sn}^{BCT_A5} = 18,358.8$	Ref. 4
${}^0L_{Bi,Sn}^{BCT_A5} = 5685.88351 - 5.5115 \times T$		Ref. 5	
${}^1L_{Bi,Sn}^{BCT_A5} = -863.7226$		Ref. 5	
CU10SN5	${}^0G_{Cu:Sn}^{CU10SN5} = -7080.1944 - 09.955536 \times T + 0.769 \times GHSERCU + 0.231 \times GHSERSN$	Ref. 4	
CU3SN	${}^0G_{Cu:Bi}^{CU3SN} = 500 + 0.75 \times GHSERCU + 0.25 \times GHSERBI$	Ref. 6	
	${}^0G_{Cu:Sn}^{CU3SN} = -8453.7781 + 0.935383 \times T + 0.75 \times GHSERCU + 0.25 \times GHSERSN$	Ref. 4	
	${}^0G_{Ag:Sn}^{CU3SN} = 5000 + 0.75 \times GHSERAG + 0.25 \times GHSERSN$	Ref. 4	
	${}^0L_{Cu:Bi,Sn}^{CU3SN} = -4693 - 7.143 \times T$	This work	
	${}^0L_{Ag,Cu:Sn}^{CU3SN} = 500$	Ref. 4	
CU41SN11	${}^0G_{Cu:Bi}^{CU41SN11} = 600 + 0.788 \times GHSERCU + 0.212 \times GHSERBI$	This work	
	${}^0G_{Ag:Sn}^{CU41SN11} = 6000 + 0.788 \times GHSERAG + 0.212 \times GHSERSN$	Ref. 4	
	${}^0G_{Cu:Sn}^{CU41SN11} = -6498.0861 - 1.06459 \times T + 0.788 \times GHSERCU + 0.212 \times GHSERSN$	Ref. 4	
	${}^0L_{Cu:Bi,Sn}^{CU41SN11} = -6938 - 1.42 \times T$	This work	
	${}^0L_{Ag,Cu:Sn}^{CU41SN11} = -50 + 8 \times T$	Ref. 4	
CU6SN5	${}^0G_{Cu:Bi}^{CU6SN5} = 100 + 0.545 \times GHSERCU + 0.455 \times GHSERBI$	This work	
	${}^0G_{Ag:Sn}^{CU6SN5} = 3000 + 0.545 \times GHSERAG + 0.455 \times GHSERSN$	Ref. 4	
	${}^0G_{Cu:Sn}^{CU6SN5} = -8036.2536 + 1.470841 \times T + 0.545 \times GHSERCU + 0.455 \times GHSERSN$	Ref. 4	
	${}^0L_{Cu:Bi,Sn}^{CU6SN5} = 2632.1 - 28.143 \times T$	This work	
	${}^0L_{Ag,Cu:Sn}^{CU6SN5} = -100$	Ref. 4	
FCC_A1	${}^0L_{Ag,Cu:Va}^{FCC_A1} = 36,772.58 - 11.02847 \times T$	Ref. 4	
	${}^1L_{Ag,Cu:Va}^{FCC_A1} = -4612.43 + 0.28869 \times T$	Ref. 4	
	${}^0L_{Ag,Bi:Va}^{FCC_A1} = 25,077.78 - 12.05475 \times T$	Ref. 5	
	${}^0L_{Ag,Sn:Va}^{FCC_A1} = 9998.4 + 6.28658 \times T$	Ref. 4	
	${}^1L_{Ag,Sn:Va}^{FCC_A1} = -44,740.4$	Ref. 4	
	${}^0L_{Bi,Cu:Va}^{FCC_A1} = 50 \times T$	Ref. 6	
	${}^0L_{Cu,Sn:Va}^{FCC_A1} = -10,309.8452 + 1.15851 \times T$	Ref. 4	
	${}^1L_{Cu,Sn:Va}^{FCC_A1} = -16,190.0328 + 6.49481 \times T$	Ref. 4	

Table II. continued

Phase	Function	Reference	
HCP_A3	${}^0L_{\text{Ag,Sn:Va}}^{\text{HCP_A3}} = 5080 + 8.05293 \times T$	Ref. 4	
	${}^1L_{\text{Ag,Sn:Va}}^{\text{HCP_A3}} = -40.5055$	Ref. 4	
	${}^0L_{\text{Ag,Cu:Va}}^{\text{HCP_A3}} = 36,772.58 - 11.02847 \times T$	Ref. 4	
	${}^1L_{\text{Ag,Cu:Va}}^{\text{HCP_A3}} = -4612.43 + 0.28869 \times T$	Ref. 4	
	${}^0L_{\text{Ag,Bi:Va}}^{\text{HCP_A3}} = 25,077.78 - 12.05475 \times T$	Ref. 5	
	${}^0L_{\text{Bi,Sn:Va}}^{\text{HCP_A3}} = 25,077.78 - 12.05475 \times T$	Ref. 5	
	${}^0L_{\text{Cu,Sn:Va}}^{\text{HCP_A3}} = 5000$	Ref. 4	
	${}^0L_{\text{Ag,Bi,Sn:Va}}^{\text{HCP_A3}} = 50,000$	Ref. 5	
	${}^1L_{\text{Ag,Bi,Sn:Va}}^{\text{HCP_A3}} = 50,000$	Ref. 5	
	${}^2L_{\text{Ag,Bi,Sn:Va}}^{\text{HCP_A3}} = 50,000$	Ref. 5	
	${}^0L_{\text{Ag,Cu,Sn:Va}}^{\text{HCP_A3}} = -5000 - 100 \times T$	Ref. 4	
	${}^1L_{\text{Ag,Cu,Sn:Va}}^{\text{HCP_A3}} = -5000$	Ref. 4	
	${}^2L_{\text{Ag,Cu,Sn:Va}}^{\text{HCP_A3}} = -5000$	Ref. 4	
	LIQUID	${}^0L_{\text{Ag,Bi}}^{\text{LIQUID}} = 3340.81 + 39.16749 \times T - 5.969876 \times T \times \ln(T)$	Ref. 5
		${}^1L_{\text{Ag,Bi}}^{\text{LIQUID}} = -5485.45 - 1.07133 \times T$	Ref. 5
		${}^2L_{\text{Ag,Bi}}^{\text{LIQUID}} = -3055.34 + 1.77449 \times T$	Ref. 5
		${}^0L_{\text{Ag,Cu}}^{\text{LIQUID}} = -22,659.1392 + 23.905039 \times T$	Ref. 4
		${}^1L_{\text{Ag,Cu}}^{\text{LIQUID}} = 1660.74 - 2.31516 \times T$	Ref. 4
		${}^0L_{\text{Ag,Sn}}^{\text{LIQUID}} = -339.49 - 31.42004 \times T + 3.081837 \times T \times \ln(T)$	Ref. 4
${}^1L_{\text{Ag,Sn}}^{\text{LIQUID}} = -18,150.65 + 5.87501 \times T$		Ref. 4	
${}^2L_{\text{Ag,Sn}}^{\text{LIQUID}} = -12,009.03 + 5.18355 \times T$		Ref. 4	
${}^0L_{\text{Bi,Cu}}^{\text{LIQUID}} = 20,747.5 - 5.85 \times T$		Ref. 4	
${}^1L_{\text{Bi,Cu}}^{\text{LIQUID}} = -4925 + 2.55 \times T$		Ref. 4	
${}^2L_{\text{Bi,Cu}}^{\text{LIQUID}} = 4387.5 - 2.3 \times T$		Ref. 4	
${}^0L_{\text{Cu,Sn}}^{\text{LIQUID}} = -15,583.768 + 40.623909 \times T - 5.6172208 \times T \times \ln(T)$		Ref. 4	
${}^1L_{\text{Cu,Sn}}^{\text{LIQUID}} = -27,739.285 + 41.927049 \times T - 4.4641876 \times T \times \ln(T)$		Ref. 4	
${}^0L_{\text{Cu,Sn}}^{\text{LIQUID}} = -13,228.943 + 0.90582783 \times T$		Ref. 4	
${}^0L_{\text{Ag,Bi,Cu}}^{\text{LIQUID}} = -42,275.9313 - 7.0348 \times T$		This work	
${}^1L_{\text{Ag,Bi,Cu}}^{\text{LIQUID}} = 11,584.9198 - 6.5624 \times T$		This work	
${}^2L_{\text{Ag,Bi,Cu}}^{\text{LIQUID}} = -11,4586.086 + 105.4876 \times T$		This work	
${}^0L_{\text{Ag,Bi,Sn}}^{\text{LIQUID}} = 4093.27 + 63.407508 \times T$		Ref. 5	
${}^1L_{\text{Ag,Bi,Sn}}^{\text{LIQUID}} = 11,188.52 - 8.978544 \times T$		Ref. 5	
${}^2L_{\text{Ag,Bi,Sn}}^{\text{LIQUID}} = 17051.3 - 21.742545 \times T$		Ref. 5	
${}^0L_{\text{Ag,Cu,Sn}}^{\text{LIQUID}} = -116,624.959 + 17.5155423 \times T$		Ref. 4	
${}^1L_{\text{Ag,Cu,Sn}}^{\text{LIQUID}} = -225,103.627 + 119.668943 \times T$		Ref. 4	
${}^2L_{\text{Ag,Cu,Sn}}^{\text{LIQUID}} = -15,633.0018 + 22.0596232 \times T$		Ref. 4	
${}^0L_{\text{Bi,Cu,Sn}}^{\text{LIQUID}} = -98,444.6354 + 73.3354888 \times T$		This work	
${}^1L_{\text{Bi,Cu,Sn}}^{\text{LIQUID}} = 4216.18869 + .0677325362 \times T$		This work	
${}^2L_{\text{Bi,Cu,Sn}}^{\text{LIQUID}} = 70,473.4648 - 70.9000423 \times T$		This work	
${}^0L_{\text{Ag,Bi,Cu,Sn}}^{\text{LIQUID}} = -28,983$		This work	

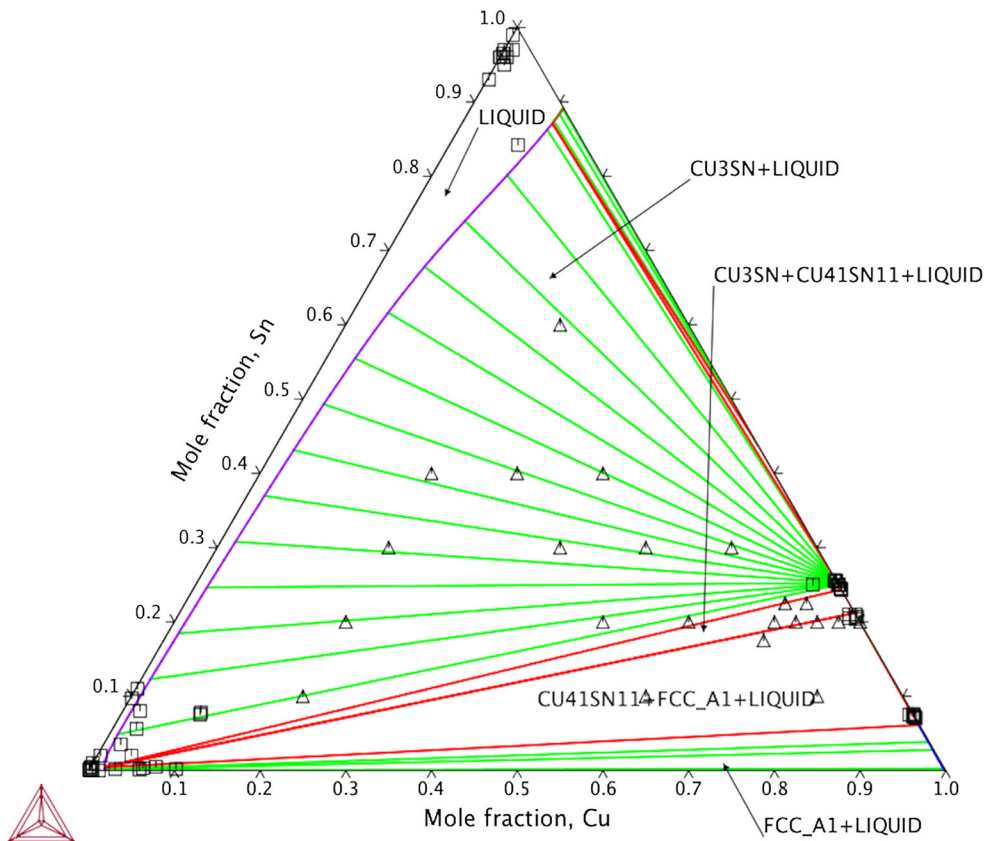


Fig. 1. Calculated isothermal section of the Bi-Cu-Sn system at 673 K superimposed with data given by Yen et al.⁷

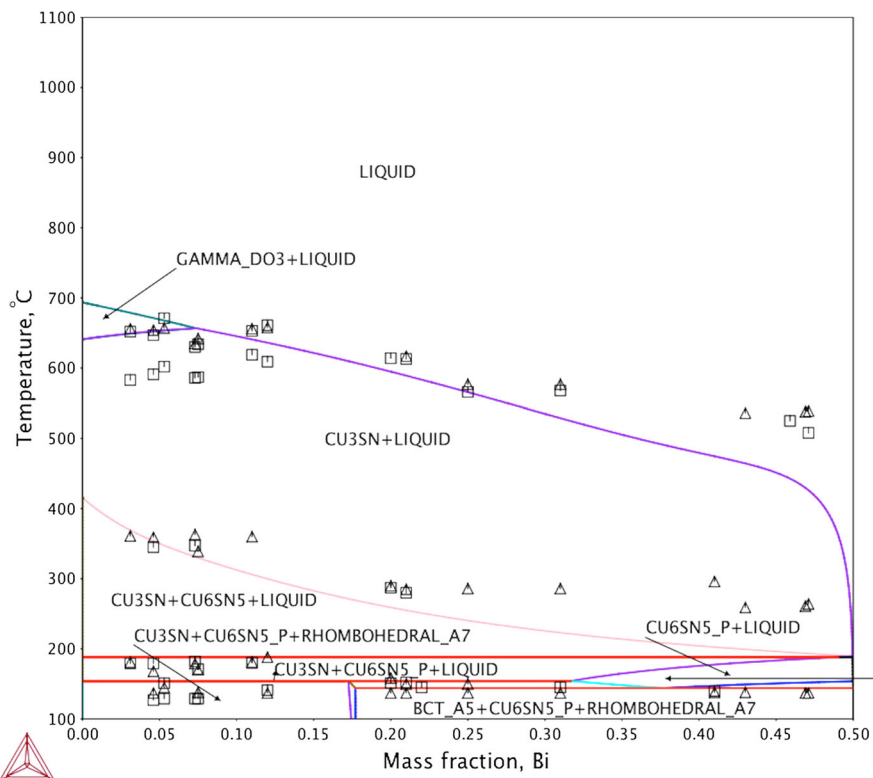


Fig. 2. Calculated isoplethal section for constant amount of Sn equals $w_{Sn} = 0.5$, together with data provided by Doi et al.⁸ Triangles represent heating, squares cooling.

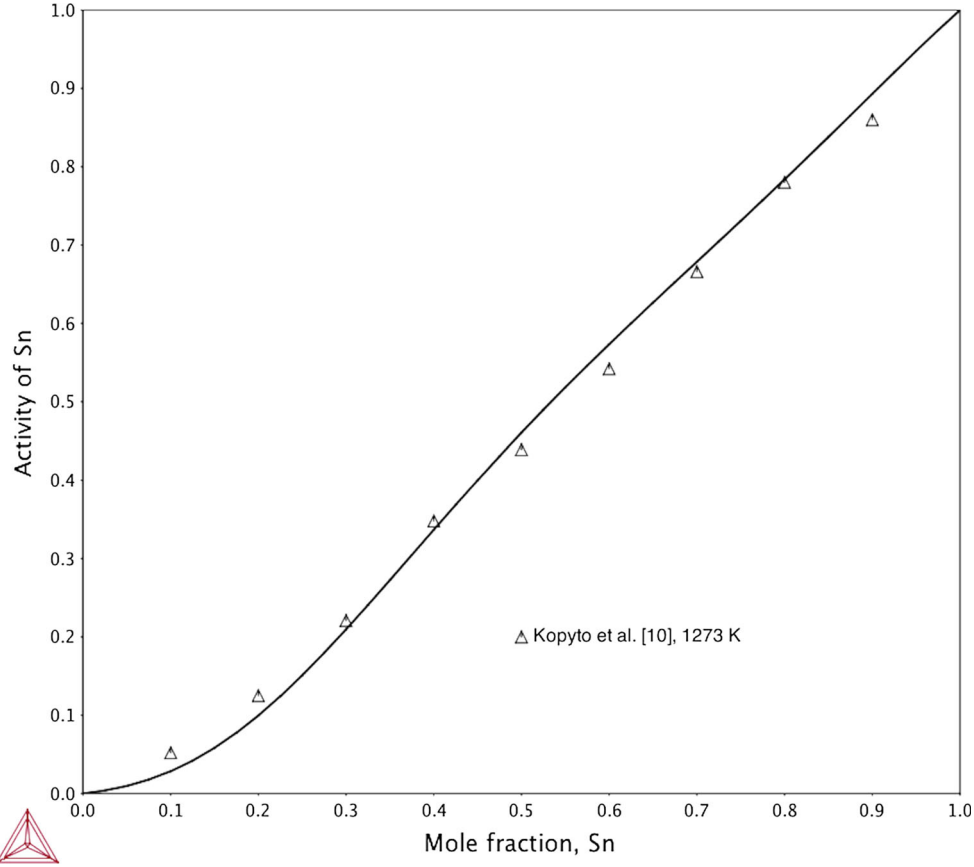


Fig. 3. Calculated activity of Sn in the Bi-Cu-Sn system at 1273 K for $x_{\text{Bi}} = x_{\text{Cu}}$, together with data given by Kopyto et al.¹⁰

$$G_m(T) = \sum_i x_i^0 G_i(T) + RT \sum_i x_i \ln(x_i) + \sum_i \sum_{j>i} x_i x_j \left(\sum_v {}^v L_{ij} (x_i - x_j)^v \right) \quad (2)$$

where the $\sum_i \sum_{j>i} x_i x_j (\sum_v {}^v L_{ij} (x_i - x_j)^v)$ part is the Redlich–Kister polynomial for excess Gibbs free energy.

Stoichiometric Compounds

Binary stoichiometric compounds $\text{Cu}_{41}\text{Sn}_{11}$, $\text{Cu}_{10}\text{Sn}_3$, are described as the line compound²⁰ using the following:

$$G_m(T) = a + b + \sum_i x_i \text{GHSE}_i \quad (3)$$

where $G_m(T)$ is the Gibbs energy of one mole of a phase, a, and b are adjustable coefficients, x_i is the mole fraction of component i , and GHSE_i is the Gibbs energy of component i in its serial element reference state.

Compound Energy Formalism Model

The Cu_3Sn , Cu_6Sn_5 , and AGSB_ORTHO phases have been described by a compound energy model.²¹ In general, the model has a form $(A, B)_i:(A, B)_j$, therefore, the Gibbs energy is given as follows:

$$G_m = Y_A^I Y_A^{II} + Y_A^I Y_B^{II} + Y_B^I Y_A^{II} + Y_B^I Y_B^{II} + iRT(Y_A^I \ln(Y_A^I) + Y_B^I \ln(Y_B^I)) + jRT(Y_A^{II} \ln(Y_A^{II}) + Y_B^{II} \ln(Y_B^{II})) + Y_A^I Y_B^I (Y_A^{II} L_{A,B:A} + Y_B^{II} L_{A,B:B}) + Y_A^{II} Y_B^{II} (Y_A^I L_{A:A,B} + Y_B^I L_{B:A,B}) + Y_A^I Y_B^I Y_A^{II} Y_B^{II} L_{A,B:A,B} \quad (4)$$

where Y_i^n represents the site fraction of element i on sublattice n , R represents the gas constant, T represents an absolute temperature, $L_{i:i,j}$ represents the interaction coefficient when mixing occurs on a second sublattice, $L_{i,j:i}$ represents the interaction coefficient when mixing occurs on a first sublattice and, $L_{i,j:i,j}$ represents the interaction coefficient when mixing occurs on both sublattices.

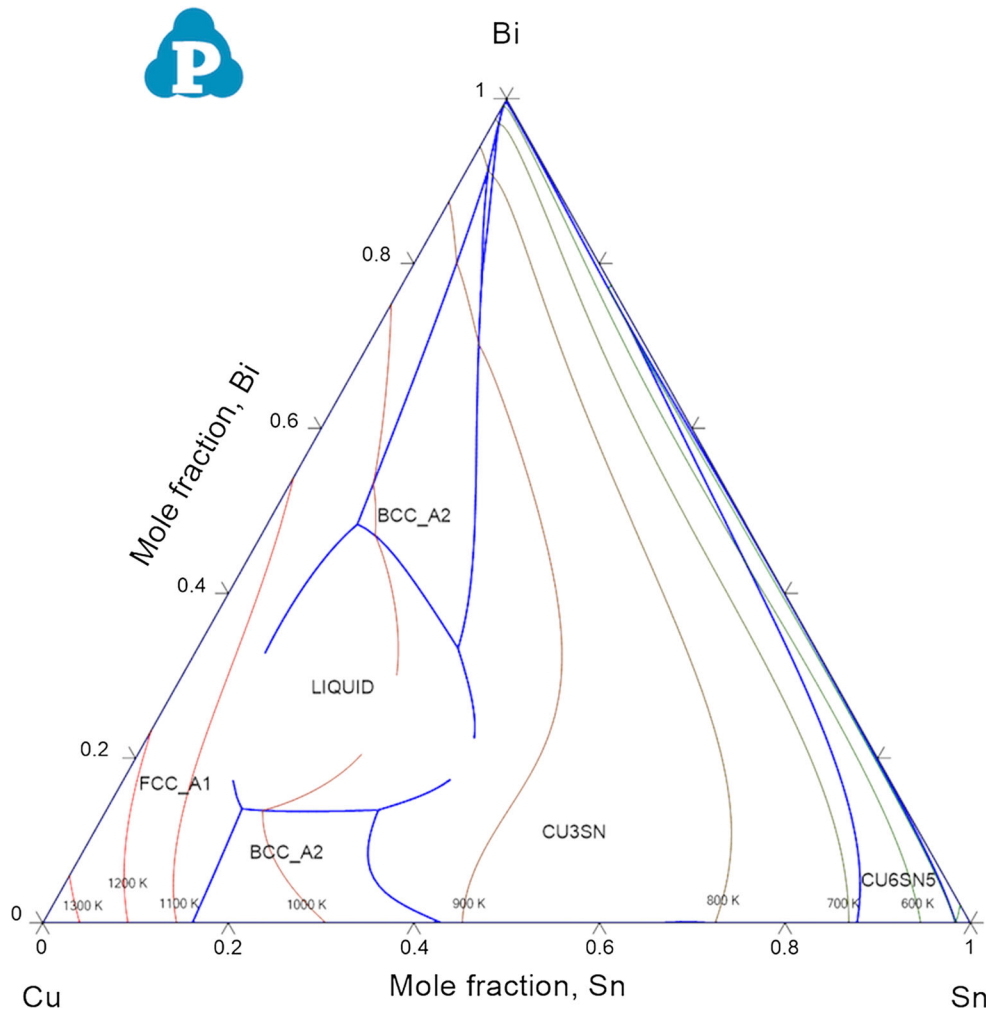


Fig. 4. Calculated liquidus projection of the Bi-Cu-Sn system.

MODELING PROCEDURE

The thermodynamic parameters for phases in the systems: Bi-Cu-Sn, Ag-Gi-Cu, and liquid phase in Ag-Bi-Cu-Sn, were optimized using ThermoCalc software.²² For this optimization, thermodynamic data for the liquid phase, invariant reactions liquidus/solidus and solid phases equilibria were used. Each piece of the selected information was given a certain weight based on experiment accuracy. The optimization was carried out step by step in agreement with Schmid-Fetzer et al.'s²³ guideline. First, the optimization of the liquid phase was performed, and then the solid phases were assessed. All parameters were finally evaluated together to provide the best description of the system. The calculated interaction parameters are shown in Table II. For checking of the results of optimization, the system was also calculated using Pandat software.²⁴

RESULTS AND DISCUSSION

The main reasons for re-optimization of the subsystems of Ag-Bi-Cu-Sn is the unification of thermodynamic models with thermodynamic descriptions previously proposed by the author, i.e., Ref. 25 or Ref. 26. In these descriptions, the focus was set not only on phase equilibria but also on precise thermodynamic modeling of the liquid. The reason of this treatment was given by Fitzner et al.²⁷ Authors of this work²⁷ showed that a thermodynamic description of the liquid phase has a great influence on extrapolation to higher-ordered systems, which is important for further applications of thermodynamic models.

The calculated Bi-Cu-Sn system at 673 K is shown in Fig. 1 together with experimental data obtained by Yen et al.⁷ It can be readily seen that the calculated results agree well with the experimental

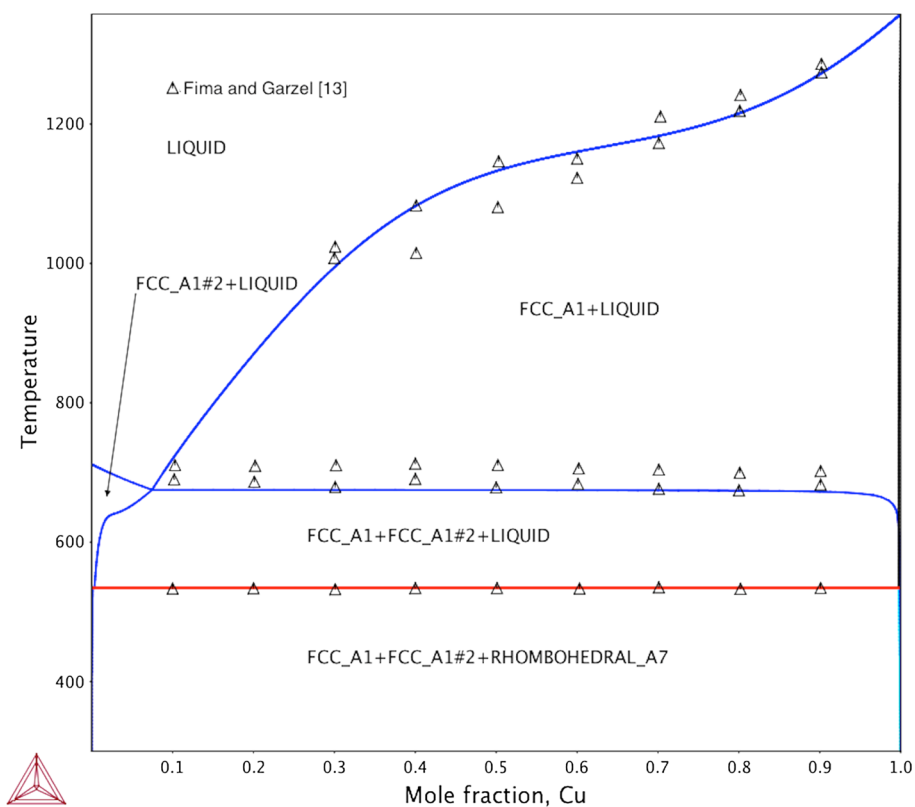


Fig. 5. Calculated isoplethal section of Ag-Bi-Cu system for $x_{Ag} = x_{Cu}$, superimposed with data given by Garzel et al.¹³

investigation.⁷ The discrepancy between the experimentally determined composition of liquid, Cu_6Sn_5 , and nominal compositions of samples can be easily explained by the experimental procedure. As was described in a previous section of this paper, Yen et al.⁷ determined the isothermal section of the Bi-Cu-Sn system by phase equilibria experiments. This kind of experiment requires keeping a sample at the desired temperature for a long time, which allows the phases to reach equilibrium. At the temperature of the experiment, the Bi-Sn part of the phase diagram is liquid, thus there is a binary equilibrium Cu_5Sn_5 -liquid. To make a compositional analysis, a sample has to be quenched from the experimental temperature to room temperature, hence the liquid phase has to be solidified. The binary Bi-Sn system reveals that, at room temperature, two solid phases, BCT_A5 and rhombohedral_A7, are virtually pure elements. Therefore, during a compositional analysis, the

information given by the BCT_A5 and rhombohedral_A7 phases cannot be applied for phase equilibria at 673 K. Moreover, due to fast quenching of the liquid phase from 673 K to room temperature, it can be assumed that non-equilibrium solidification occurred, which explains the scattered compositions of BCT_A5 and rhombohedral_A7 obtained by Yen et al.⁷

Figure 2 shows the calculated isoplethal section of the Bi-Cu-Sn system for a constant concentration of Sn equal to 0.5 weight fraction. In the same figure, one can find experimental data given by Doi et al.⁸ In general, the calculation agrees with the experimental; however, the calculated liquidus line lies lower than that of the experiment for high concentrations of Bi. This can be explained by the influence of the binary Bi-Sn system onto ternary. In other words, the thermodynamic description of Bi-Sn used in this work “pushes” the liquidus

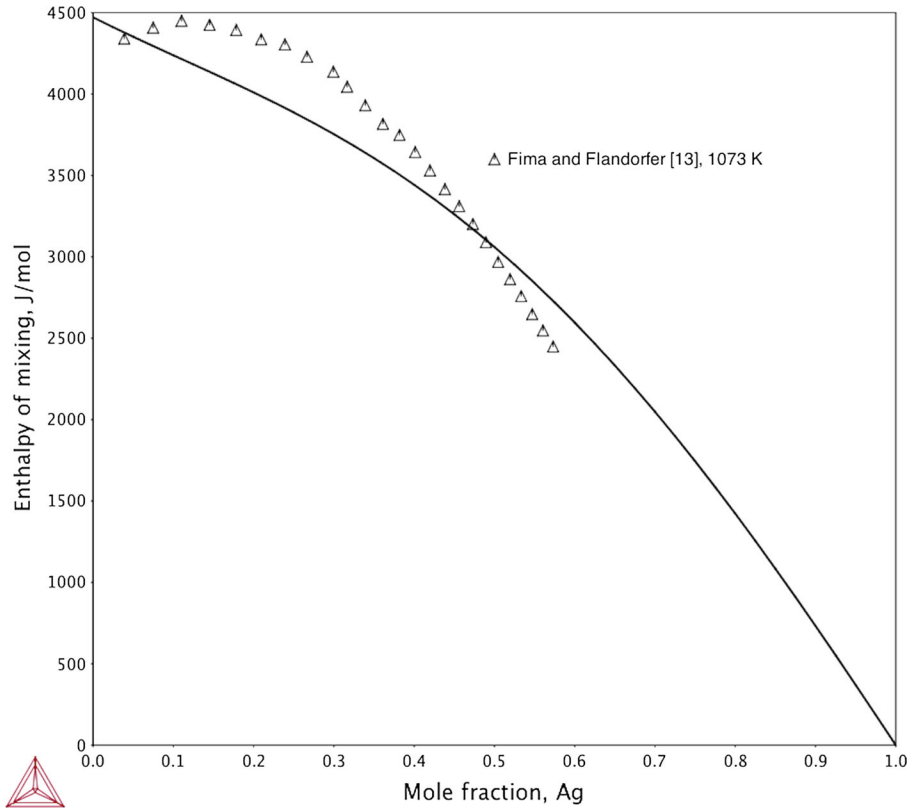


Fig. 6. Calculated enthalpy of mixing in liquid Ag-Bi-Cu at 1073 K for intersection $x_{\text{Bi}} - 1.86 \times x_{\text{Cu}} = 0$, together with data given by Fima and Flandorfer.¹⁴

surface towards lower temperatures for concentrations with small amounts of Cu, which is a consequence of Muggianu extrapolation.²⁸ On the other hand, applying too large a ternary interaction parameter will have significant influence on thermodynamic properties, as was shown by Janz and Schmid-Fetzer.²⁹ Nevertheless, to keep consistency with previous descriptions,⁵ it was decided to not change the interaction parameters in a binary liquid Bi-Sn alloy.

Figure 3 shows the calculated activity of Sn at 1273 K for intersection $x_{\text{Bi}} = x_{\text{Cu}}$, together with experimental data provided by Kopyto et al.¹⁰ It can be seen that the calculated results agree with those of the experiment and shows a negative deviation from Raoult's Law for the whole concentration range.

Figure 4 shows the calculated liquidus projection of the ternary Bi-Cu-Sn system. One can see that the calculation shows a miscibility gap in the liquid phase, which is opposite to the results obtained by Kattner⁹; however, the miscibility gap was confirmed by the results provided by Doi et al.⁸ who determined the liquid separation by DSC experiment, and by Flandorfer et al.¹² who found constant enthalpy of mixing of the liquid phase which confirms the miscibility gap.

The calculated isoplethal section of the ternary Ag-Bi-Cu system for $x_{\text{Ag}} = x_{\text{Cu}}$ is shown in Fig. 5. In the same figure, the experimental data obtained from DTA analysis by Fima and Garzel¹³ are presented. One can see that the calculated phase diagram agrees well with the thermal analysis investigation.¹³

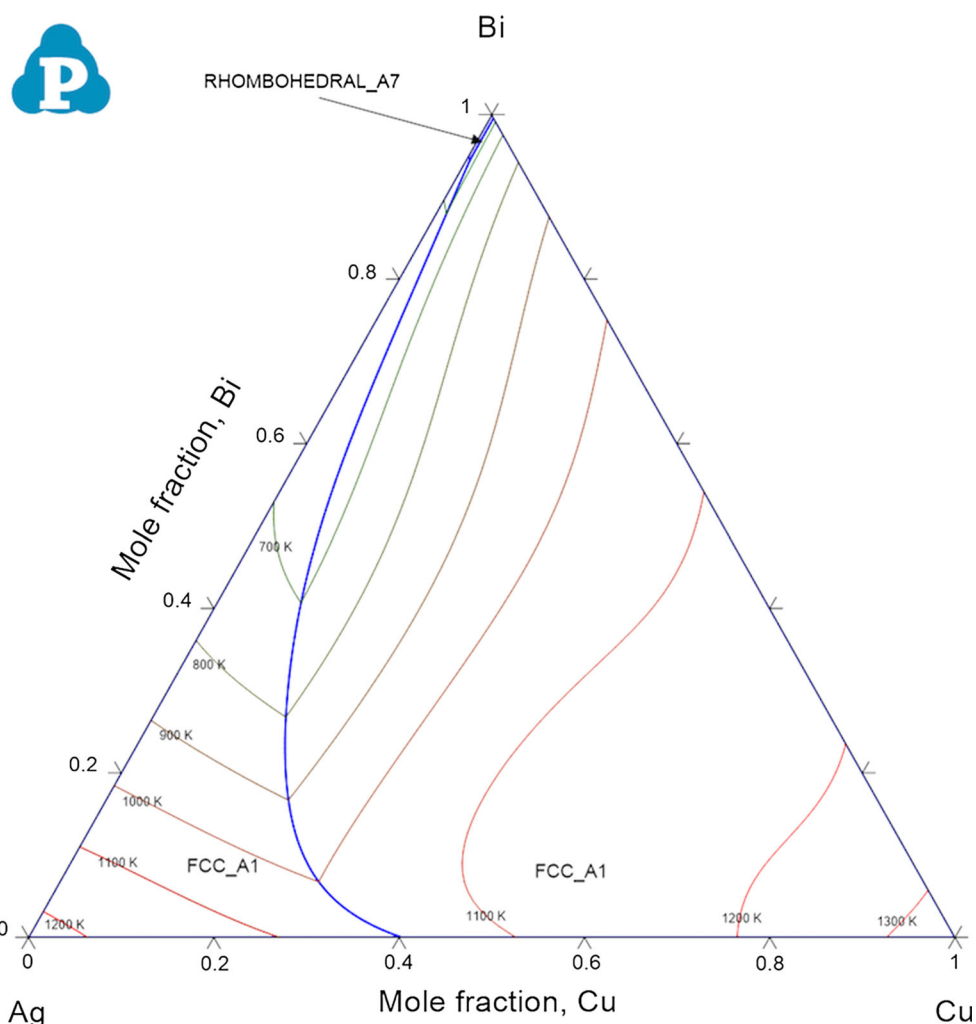


Fig. 7. Calculated liquidus projection of the Ag-Bi-Cu system.

Figure 6 shows the calculated liquid enthalpy of mixing at 1073 K for intersection $x_{\text{Bi}} - 1.86x_{\text{Cu}} = 0$. In general, the calculation agrees with the literature data¹⁴ within experimental error. It should be noticed that, for concentration Ag equals 0, the calculated function starts from a binary Bi-Cu that has been taken from the COST531 database.⁶ Extrapolation of the experiment into binary system will give a value of enthalpy equals 4100 J/mol, what is ca. 400 J/mol less than a value retrieved from the COST 531 database. A similar discrepancy can be found for the concentration of Ag equals 0.2 mol fraction. Considering a typical calorimetry measurement error, this kind of difference between modeling and experiment is acceptable.

Figure 7 exhibits the calculated liquidus projection of the ternary Ag-Bi-Cu system. It can be easily seen that, almost for the whole concentration range, the primary solidification is FCC_A1 phase; however, with different composition sets: Ag-rich and Cu-rich, the rhombohedral_A7 is a primary solidification phase only for a tiny region located in the Bi-rich corner of the phase diagram.

Figure 8 displays the calculated activity of Sn in a quaternary liquid for intersection $x_{\text{Cu}} = x_{\text{Ag}} = x_{\text{Bi}}$ at 1273 K, superimposed with data given by Garzel et al.¹⁵ One can see that the calculated activity reproduces experimental data quite well.

Figure 9 shows the calculated isoplethal section of the quaternary Ag-Bi-Cu-Sn system for constant

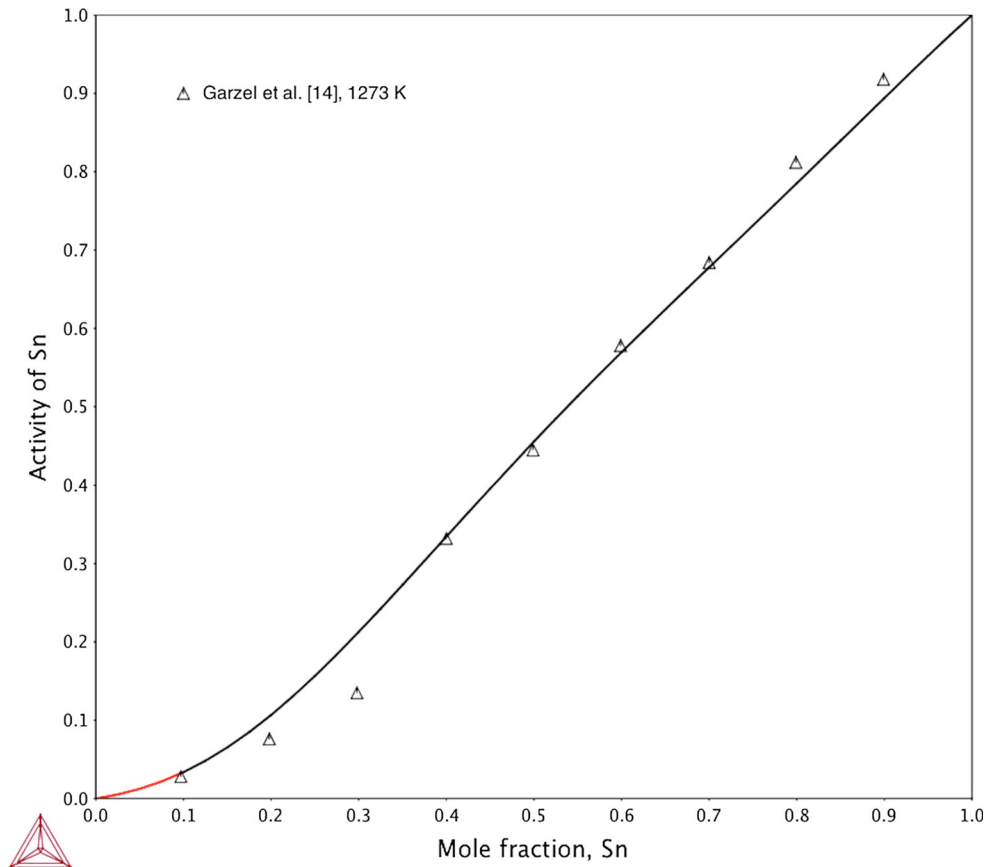


Fig. 8. Calculated activity of Sn in quaternary Ag-Bi-Cu-Sn at 1273 K for intersection $x_{\text{Cu}} = x_{\text{Bi}} = x_{\text{Ag}}$, together with data provided by Garzel et al.¹⁵

amounts of Ag equals 2 wt.% and Cu equals 0.7 wt.% superimposed with experimental data given by Doi et al.⁸ The agreement between calculation and experiment is good. The calculated liquidus line is located at a slightly higher temperature than the experiment for small amounts of Bi; however, for larger amounts of Bi, the calculation lies between the scattered experimental points.

Figure 10 shows phase fractions during the solidification of the alloy Sn-2 wt.% Ag-6 wt.% Bi-0.5 wt.% Cu. An alloy with this composition was proposed by Wu et al.¹⁵ as a new lead-free solder. It can be seen that the majority of the solid is the BCT_A5 phase with a small addition of the AgSb_Ortho phase (IMC Ag₃Sn). One can also find

a small amount of Cu₆Sn₅ phase inside the solder; however, the amount of Cu₆Sn₅ is limited and equals 1.3%. The calculated melting point of the Sn-2 wt.% Ag-6 wt.% Bi-0.5 wt.% Cu alloy equals 487 K, which is 4° higher than that determined by Wu et al.¹⁵

SUMMARY

The thermodynamic model of a quaternary Ag-Bi-Cu-Sn system was obtained by aid of the Calphad approach. Good agreement between the calculations and experimental data was found. The thermodynamic database can be easily used for extrapolation to higher-ordered systems.

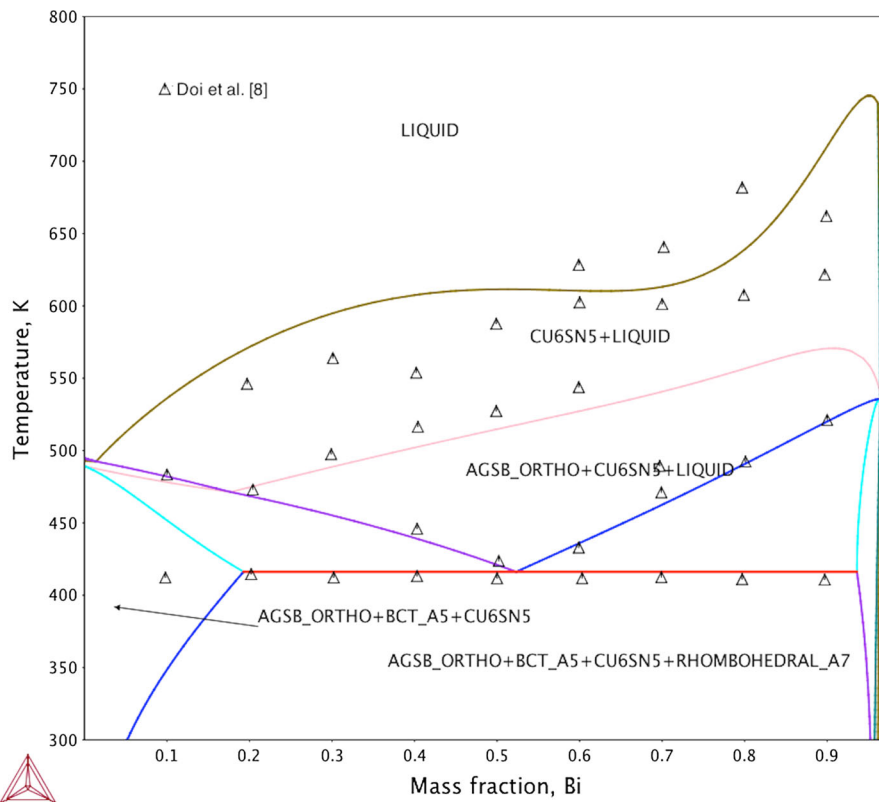


Fig. 9. Isolethal section of Ag-Bi-Cu-Sn system for constant amounts of Ag equals 2 wt.% and Cu equals 0.7 wt.%, superimposed with data given by Doi et al.⁸

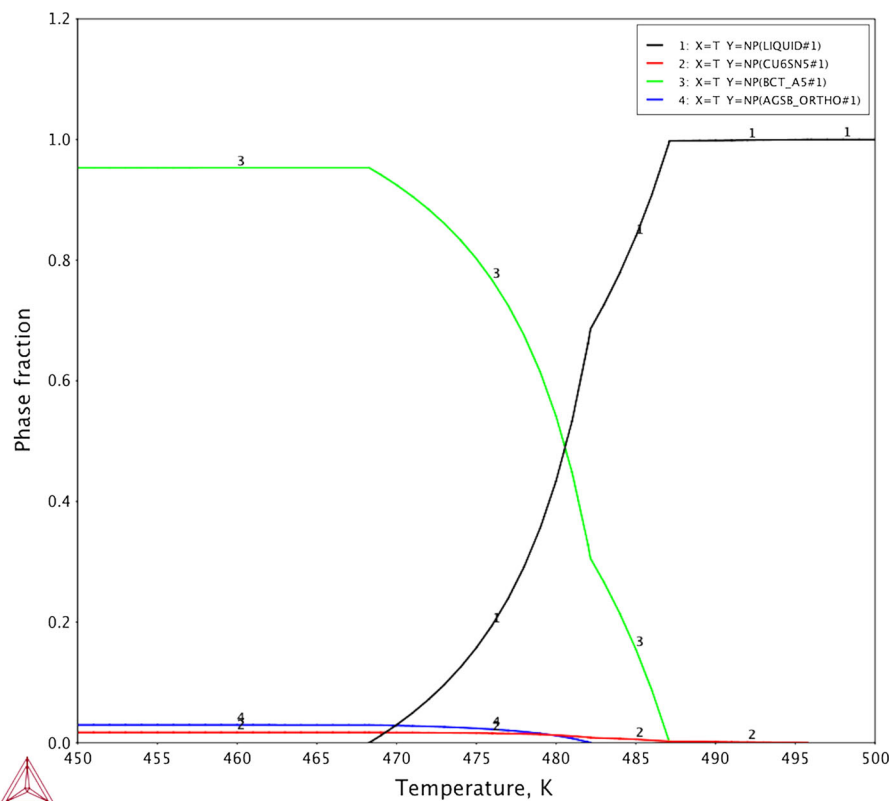


Fig. 10. Calculated site fraction of phases during the solidification of alloy Sn-2 wt.%Ag-6 wt.%Bi-0.5 wt.%Cu.

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