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ORIGINAL RESEARCH ARTICLE

Measurement of Mixing Enthalpies for Sn-Bi-Sb Lead-Free Solder System

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Abstract

Predictions of the thermodynamic behavior of higher-order multicomponent alloys from thermodynamic data of binary and ternary systems have been proven to be very crucial, as it is extremely challenging to investigate the thermodynamic properties of higher-order systems. Therefore, it is necessary to assess the thermodynamic data of various binary and ternary systems that are important to lead-free solder applications. The literature lacks thermodynamic information for some lead-free systems. Tin–bismuth–antimony (Sn-Bi-Sb) is a good option as a solder ternary system free of lead. The integral and partial mixing enthalpies of a Sn-Bi-Sb system were determined using a drop-solution calorimeter. At 923 K, 973 K, and 1023 K, calorimetric measurements of the Sn-Bi-Sb system were made along five of the cross-sections. Pieces of pure tin were dropped into molten $Sb_{0.25}Bi_{0.75}$, $Sb_{0.50}Bi_{0.50}$, $Sb_{0.75}Bi_{0.25}$ alloys, bismuth into $Sb_{0.50}Sn_{0.50}$, and antimony into $Bi_{0.50}Sn_{0.50.}$ Using the calorimetric data, partial and integral thermodynamic properties were determined. The integral mixing enthalpy was used to plot iso-enthalpy curves. It was found that the mixing enthalpies were temperature-independent. The substitutional solution Redlich–Kister–Muggianu model was used to derive the interaction parameter based on ternary enthalpy values and, to obtain these parameters, a least square fitting model was used. When the estimated and measured values were compared, it was found that there was a good agreement between them.

Keywords Lead-free solders · Sn-Bi-Sb system · mixing enthalpy · ternary · thermodynamic modeling · drop calorimeter

Introduction

The best soldering materials in the electronics sector are lead–tin alloys because of their exceptional mechanical, chemical, and physical properties. They are very reliable and easily manufactured and have dominated the soldering industry for many years without much improvement. However, finding a new alternative solder alloy to replace lead has been difficult due to its excellent properties except for its environmental and health hazards. Due to the development of advanced technology, most of the electronic items, including mobile phones, etc., have been miniaturized. This technology has grown and advanced quite quickly. Electronic products lose their effectiveness after a short span of time, so, as a result, a lot of electronic garbage is produced.[1–8] The majority of old gadgets are thrown away in landfills, where the lead eventually seeps into the soil and contaminates the groundwater. The European Union is making great efforts to enforce a lead ban on devices. In June 2000, the EU approved the Waste of Electrical and Electronic Equipment Directive and the Regulation on the Restrictions of the Use of Certain Hazardous Substances.[9,10] There is a big motivation in the electronic industry to shift from lead–tin to lead-free solders. In recent years, electronic assembly manufacturing has undergone considerable modifications. To enable lead-free solder in electronics, some manufacturers have already begun to adapt the design. Accurate phase diagram determination and thermodynamic property measurements are the initial stages in the creation of novel solder alloys (lead-free). Many experts in this field have suggested the creation of a thermodynamic database for solder systems that are free of lead, which is why it is very important to carry out experiments on this type of alloy system to generate a reliable database of their thermodynamic properties.

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Literature Survey

Bi-Sn System

Several researchers have conducted experimental investigations on the phase equilibria and thermodynamic characteristics of this system, but there is a significant discrepancy in some of the findings. The specific heat was measured by Nagasaki and Fujita[11] and the heat of mixing was calculated by Oelsen and Golucke.[12] Ohtani and Ishida,[13] who tested the eutectic temperature using differential scanning calorimetry, more recently released liquidus data. These data generally agree well with one another. Numerous writers have also looked at the mixing enthalpies of liquid Bi-Sn alloys, including.[14–17] As noted by Ohtani and Ishida,[13] research done prior to the 1940s[14] exhibits significant scatter, but later data[15–17] exhibit rather good agreement. Electromotive force (EMF) techniques have been used by numerous authors to measure the activities of Sn in the liquid phase; Asryan and Mikula's contribution[18] is one of the most recent efforts in this area. Bi in the liquid bath of Sn was also measured by Yazawa and Koike[19] at 1100 °C, while Rickert et al.[20] did so between 750 °C and 1050 °C. The activities were measured by the several authors and there was good agreement; however, the calculated enthalpies revealed significant disparities between them. Only Seltz and Dunkerley's models[21] had good agreement with the data that were directly measured.[15–17] Enthalpies of formation are also different from Oelsen and Golucke's calorimetric observations.[12] The study by Lee et al.[22] contains a list of other important sources.

Sb-Sn Binary System

The literature has several calorimetric analyses of the enthalpy of mixing of liquid Sb-Sn alloys. Kawakami[23] was the first to record it, in 1930, at 800 °C. Later, Kleppa[24] did so at 450 °C and 700 °C. All these facts have been included in Hultgren et al compilation's.[25] Later, Sommer et al.[26] and Azzaoui et al.[27] calculated the enthalpy of mixing of liquid alloys in the temperature range of 510–835 °C, and at 619 °C ($0.5 \le x_{Sn} \le 1$) and 640 °C ($0 \le x_{Sn} \le 0.5$), respectively, to come to the ultimate conclusion that all the experimental results were satisfactory. Sommer et al.[26] proposed a minor but considerable temperature dependence of H_{mix} and the formation of two compounds, SbSn and $SbSn_2$. Frantik and Mcdonald[28] and Vassiliev et al.[29] used EMF methods to calculate the relevant H_{mix} values. Recent research by Chen et al.[30] utilizing a regular solution model, and the assumption of temperature-independent heat of mixing, defined the liquid phase in the Sb-Sn system. The computed values and the experimental results published by Wittig et al.,[15] Sommer et al.,[26] and Azzaoui et al.[27] are in good agreement.

Bi-Sb Binary System

The binary system Bi-Sb, which features an equilibrium between solid and liquid solutions, is only briefly discussed in a few papers. Hansen and Anderko[31–33] established a phase diagram, with a liquidus and a solidus that were somewhat less precisely known. The well-known works of Hultgren et al.[25] and Smithells et al.[34] both cite these findings. For alloys with a composition of $x_{Sb} = 0.21–0.77$ and at a temperature of 1073 K, Kawakami et al.[4,23] calculated the enthalpy of formation through the direct reaction method. At a temperature of 298 K, Kubaschewski and Seith[35] found the mixing temperatures of the constituents in the solid state. Geguzin and Pines[36] explored solid solutions in the binary Bi-Sb system. For the alloy with $x_{Sb} = 0.63$ in the temperature range of 623–823 K, they calculated the specific heat.

Sn-Bi-Sb Ternary System

Katayama et al.[37] employed the fused salt EMF method to obtain the activity of tin between 700 K and 1000 K along pseudo-binary sections of Sn(x_{Sb}/x_{Bi} = 1/3, 1/1 and 3/1) and in binary alloys of Sn-Sb and Sn-Bi systems. Based on these findings, Darken's equation was used to determine the concentration dependence of the excess Gibbs energy of mixing. Manasijevic et al.[38] examined phase equilibria in the Sn-Bi-Sb ternary system using phase diagram calculations as well as experimental results.

Awe et al.[39] studied the thermodynamic activity of Sn in the ternary lead-free solder system (Sn-Bi-Sb) at 900 K using a molecular interaction model and predicted the activities of all the components in Sn-Bi-Sb along three cross-sections from the corner of each metal with a molar ratio of the other two components (1:3, 1:1, and 3:1) in the temperature range of 500–1000 K.

Zhang et al.[40] studied the effect of Sb content on the properties of Sn-Bi solders and found that the shear strength of Sn-Bi-Sb solders increases as the Sb content increases. This alloy has a wider melting range because it is highly sensitive to Sb content. Also as the Bi content decreases and the Sb content increases, the alloy showed more ductility. So, the literature review suggests that the thermodynamic properties like activities and Gibbs free energy of Sn-Bi-Sb were predicted by using different computational modeling and EMF measurement techniques, but no enthalpy data are available for the entire composition range for the given Sn-Bi-Sb system.

Therefore, calorimetric measurements of the Sn-Bi-Sb system have been carried out along five of the cross-sections (see Fig. 1) in the temperature range of 923–1023 K using a calorimeter (96 Line Evo; Setaram Instruments, France), as set out in the "Calorimetric Measurements" section, below.

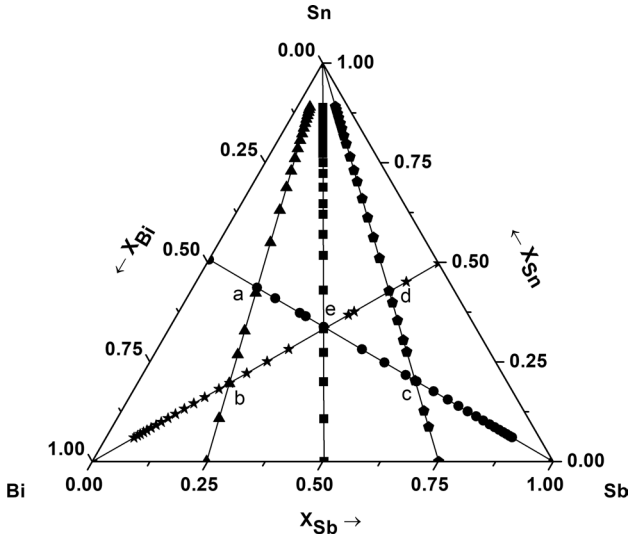

Fig. 1 Measured cross-sections (intersections *a* to *e* indicated; see Table V, below) and alloy compositions in the Sn-Bi-Sb ternary system.

Partial and integral thermodynamic properties were determined from the calorimetric data. Integral mixing enthalpy plots were used to generate iso-enthalpy curves. The substitutional solution Redlich–Kister–Muggianu (RKM) model was used to derive the interaction parameter based on ternary enthalpy values, and, to obtain these parameters, a least square fitting model was used. Comparisons are made between the estimated and measured values.

Experimental

Materials

The binary and ternary alloys formed in this study were made from pure metals (Sn, Bi, and Sb). α-Al_2O_3 needles from the National Institute of Standards & Technology (NIST; Gaithersburg, MD, USA), were used as the calibration reference. The metals were cleaned with n-hexane in a supersonic bath and then vacuum-dried in a glove box antechamber to eliminate any remaining solvent. They were then divided into small bits and precisely weighed to the accuracy of 10^{-4} g. Table I lists the specifications for the pure metals and argon (protective gas).

Calorimetric Measurements

In this investigation, the drop calorimeter was used to obtain the enthalpy values of the given system. It is equipped with a furnace of resistance-type made up of a graphite tube, and having an arrangement for the flow of water throughout the outer section of the furnace for continuous cooling and a thermopile of 56 pairs of S-type thermocouples. The furnace could operate at a maximum temperature of 1593 K. It has a motorized dropping apparatus that helps in dropping the metals automatically into the crucible, which had an outer diameter of 12 mm and length of 60 mm. For the calibration of the calorimeter, four pieces of NIST SRM 720 α-Al_2O_3 needles were dropped at the end of each sample series. The these needles were certified by NIST as adhering to its standards. CALISTO Data Processing software was used to monitor the calorimeter. A specified amount of base metal was added to the crucible before the trials began. The CALISTO software managed the flow of gas and the water-cooling system. Prior to the start of the trials, everything needs to be programmed, such as the rate of heating and cooling, how time the temperature needed to be held for, and the rate of gas flow. To create a completely inert atmosphere, all the air was flushed out of the crucible and the protective tube (the space between outer and inner walls of the furnace) by using a vacuum pumping system and then argon gas was passed through the crucible. Throughout the studies, a steady supply of argon (about 30 mL/min) kept the alloy inert from oxidizing. Argon also took the fumes arising from the heating process from the furnace, and so behaved as a carrier gas as well as a protective gas. There was a 30-min gap between two successive drops and then the heat signals were recorded. At 923 K, 973 K, and 1023 K, calorimetric analyses of the Sn-Bi-Sb system were conducted along five of the cross-sections (see Fig. 1). Pieces of pure tin were dropped into molten $Sb_{0.25}Bi_{0.75}$, $Sb_{0.50}Bi_{0.50}$, $Sb_{0.75}Bi_{0.25}$ alloys. bismuth into $Sb_{0.50}Sn_{0.50}$, and antimony into $Bi_{0.50}Sn_{0.50}$. Prior to introducing the sample material, the system underwent a roughly 16-h thermal equilibration process to establish a stable baseline. The entire mass of the crucible and the samples were weighed before and after the measurements to confirm that there was only a little weight loss due to evaporation. Each experiment was repeated twice while holding the parameters constant. The CALISTO software was then used to integrate the recorded heat signals and estimate the enthalpy values.

Table I The materials used for this study

Materials	Initial purity (wt%)	Source
Argon gas	~ 99 (vol%)	Indian Oxygen, India
Antimony (lumps)	99.999	Johnson Matthey, UK
Bismuth (lumps)	99.999	Johnson Matthey, UK
Tin (shots)	99.999	Johnson Matthey, UK

Results and Discussion

With the aid of the CALISTO software, the heat flow curves' peaks were integrated. The heat signal value associated with the α-Al_2O_3 needle drops served as the basis for determining the calibration constant (K). After being multiplied by the calibration constant, the integral values of each heat signal were then converted to enthalpy, which is known as the heat effect. Here, the reaction enthalpy ($\Delta H_{\mathrm{Reaction,X,i}}$) which is a function of heat effect ($\Delta H_{\mathrm{Signal,X,i}} \cdot K$) and the change in enthalpy ($\Delta H_{\mathrm{X,i}}^{T_{\mathrm{D}} \to T_{\mathrm{M}}}$), is calculated by Eq. 1 when species X is dropped from the drop temperature (T_{D}) to the bath temperature (T_{M}):

$$\Delta H_{\mathrm{Reaction,X,i}} = \left(\Delta H_{\mathrm{Signal,X,i}} \cdot K\right) - \left(\Delta H_{\mathrm{X,i}}^{T_{\mathrm{D}} \to T_{\mathrm{M}}} \cdot n_{\mathrm{X,i}}\right) \quad (1)$$

where $n_{\mathrm{X,i}}$ represents the amount of species X (no. of moles) which was dropped by the help of automatic dropping device into the liquid bath and, corresponding to every peak, there is a $\Delta H_{\mathrm{Signal,X,i}}$ value which is the integrated area (μV/s) after integrating the peaks corresponding to each drop by using the baseline integration tool. $\Delta H_{\mathrm{X,i}}^{T_{\mathrm{D}} \to T_{\mathrm{M}}}$ represents the change in the molar enthalpy of species X and this change can be calculated by the help of enthalpy data available in the literature for each species corresponding to a given temperature range.

Equation (2) can be used to calculate the partial enthalpy $\Delta \overline{H}_{\mathrm{X,i}}$ as a very small amount of species X was added to liquid metal in the crucible:

$$\Delta \overline{H}_{\mathrm{X,i}} \approx \Delta H_{\mathrm{Reaction,X,i}} / n_{\mathrm{X,i}} \quad (2)$$

Each measurement involved adding specific amounts of one of the three metals to the crucible, then dropping the remaining two metals at the specified temperature. Thus, Bi was placed into the crucible and Sb was then dropped, and then Sn was dropped into the binary Bi-Sb; next, Sb was placed into the crucible and Sn was then dropped and then Bi was dropped into the binary Sb-Sn; and finally Sn was placed into the crucible and Bi was then dropped and then Sb was dropped into the binary Bi-Sn. According to Eq. 3, the integral molar mixing enthalpy ΔH_{mix} is computed as:

$$\Delta H_{\mathrm{mix}} = \frac{\sum \Delta H_{\mathrm{Reaction}}}{\left(n_{\mathrm{crucible}} + \sum n_{\mathrm{i}}\right)} \quad (3)$$

The Bi, Sn, and Sb enthalpy increments from room temperature to the drop temperature were acquired from the literature[25,41] and used in Eq. 1. Tables II, III, and IV provide the molar integral enthalpies which were derived by the help of Eq. 3 for the given ternary system along five sections considering various compositions. They additionally include partial mixing enthalpies values with the variation in the composition of the different species.

Errors in calorimetric measurements can come from a number of different places, including the calorimeter's construction type, calibration, heat flow curve baseline integration, degree of solute solubility in the solvent, and impurity concentration. The calorimeter's overall experimental uncertainty ranges from 10 to 12%. It was determined that the calibration error caused by the dropping α-Al_2O_3 needles was less than ± 1.5%.

The enthalpies of mixing of the five cross-sections depicted in Fig. 1 in the Sn-Bi-Sb ternary system were determined at 923 K, 973 K, and 1023 K. Pieces of pure tin were dropped into molten $Sb_{0.25}Bi_{0.75}$, $Sb_{0.50}Bi_{0.50}$, $Sb_{0.75}Bi_{0.25}$ alloys; bismuth into $Sb_{0.50}Sn_{0.50}$, and antimony into $Bi_{0.50}Sn_{0.50}$ alloys. The closeness of readings near the intersection points on the five cross-sections indicates the quality of our experimental data (see Table V; Fig. 1). In each attempt, the variation was significantly reduced and hardly noticeable. However, systemic errors, such as those resulting from insufficient mixing reactions, cannot be completely ruled out.

Figure 2 illustrates the change in mixing enthalpies for three different isopleths and two binaries. For the three isopleths and the Sb-Sn binary, the mixing enthalpies are exothermic across the Sn composition, but endothermic at the low-Sn composition end. For these three cross-sections, it was found that the mixing enthalpy's minima was exothermic in nature which makes the alloy more stable.

Mixing enthalpy's minima corresponding to the cross-sections $(Sb_{0.25}Bi_{0.75})_{1-x}Sn_x$ is close to x_{Sn} ~ 0.62 and for the cross-section $(Sb_{0.50}Bi_{0.50})_{1-x}Sn_x$ is approximately equal to x_{Sn} ~ 0.55 and. if we consider the cross-section $(Sb_{0.75}Bi_{0.25})_{1-x}Sn_x$, it is almost symmetric about the tin composition.

The enthalpy of mixing falls with increasing tin content and reaches a minimum at the tin composition indicated above. As the $x_{\mathrm{Sb}}/x_{\mathrm{Bi}}$ ratio decreases, it can also be seen in Fig. 2 that the lowest value (minima) in the curve representing mixing enthalpy becomes less exothermic in nature, and reaches its peak at equi-atomic composition after which it decreases at the extremes. The Bi, Sb, and Sn atoms' interatomic interaction may have diminished as a result.

Regardless of the mixing entropy's sign, the mixing enthalpy adds adversely to the Gibbs energy for the majority of the tin composition. The measured mixing enthalpy is found to be negative which suggests that the atoms in this system have finite amounts of interatomic interaction energy. This indicates that the heat is produced by a mixing process making it more exothermic.

Figures 3, 4, and 5 illustrate the nature of mixing enthalpies with the variations in the composition of Sn. Additionally, it can be seen that the enthalpy curves at

Table II Integral and partial mixing enthalpies of Sn-Bi-Sb alloys when Sn dropped

Added moles	Mole fraction (x_{Sn})	Standard uncertainties u(x_{Sn})	Heat effect $H_{signal}{\cdot}K$ (J)	Standard uncertainties $u(\Delta H_{signal}{\cdot}K)$ (J)	Heat of reaction $\Delta H_{reaction}$ (J)	Partial enthalpy $\Delta\overline{H}_{X,i}$ (J mol^{-1})	Integral enthalpy $\Delta \boldsymbol{H}_{\mathbf{mix}}$ (J mol^{-1})
Series 1: $(Sb_{0.25}Bi_{0.75})_{1-x}Sn_x$ alloys; atmosphere: argon at pressure $p = 0.1$ MPa; starting amount $n_{Bi} = 0.002586$ mol, $K = 0.001899$ JμVs^{-1}, $T_D = 298$ K, $T_M = 923$ K, $\Delta H_{Sn}^{T_D \to T_M} = 24115$ (J mol^{-1}),$\Delta H_{Sb}^{T_D \to T_M} = 37089.563$ (J mol^{-1});							
n_{Sb}							
0.000853	0	0.0002	33.067	0.005	1.430	1676	415.886
n_{Sn}							
0.000489	0.1245	0.0007	11.523	0.005	− 0.269	− 550	295.527
0.000486	0.2209	0.0004	11.333	0.009	− 0.387	− 796	175.399
0.000391	0.2843	0.0002	8.980	0.011	− 0.449	− 1148	67.535
0.000421	0.3419	0.0001	9.736	0.014	− 0.416	− 988	− 17.449
0.000853	0.4343	0.0003	20.123	0.007	− 0.447	− 524	− 88.479
0.001567	0.5502	0.0005	36.966	0.014	− 0.822	− 525	− 177.930
0.001613	0.6286	0.0004	38.343	0.007	− 0.554	− 343	− 206.679
0.001637	0.6844	0.0005	39.285	0.015	− 0.191	− 117	− 193.219
0.001579	0.7243	0.0003	37.906	0.011	− 0.172	− 109	− 182.528
0.002081	0.7637	0.0007	50.045	0.013	− 0.138	− 66	− 165.912
0.001555	0.7865	0.0005	37.436	0.014	− 0.063	− 41	− 153.819
0.001707	0.8070	0.0004	41.075	0.015	− 0.089	− 52	− 144.088
0.001489	0.8219	0.0001	35.605	0.013	− 0.302	− 203	− 148.610
0.002082	0.8392	0.0003	50.318	0.012	0.111	53	− 128.931
0.001572	0.8502	0.0004	38.074	0.004	0.165	105	− 112.932
0.001643	0.8602	0.0006	39.334	0.002	− 0.287	− 175	− 117.055
0.001504	0.8683	0.0003	36.536	0.013	0.267	178	− 100.101
0.001716	0.8764	0.0001	41.346	0.014	− 0.035	− 20	− 95.160
0.002339	0.8860	0.0002	56.133	0.007	− 0.272	− 116	− 96.814
0.002044	0.8932	0.0004	49.595	0.015	0.304	149	− 81.236
Series 2: $(Sb_{0.25}Bi_{0.75})_{1-x}Sn_x$ alloys; atmosphere: srgon at pressure $p = 0.1$ MPa; starting amount $n_{Bi} = 0.002593$ mol, $K = 0.001911$ JμVs^{-1}, $T_D = 298$ K, $T_M = 973$ K, $\Delta H_{Sn}^{T_D \to T_M} = 26351$ (J mol^{-1}), $\Delta H_{Sb}^{T_D \to T_M} = 38658.938$(J mol^{-1})							
n_{Sb}							
0.000855	0	0.0003	34.494	0.011	1.441	1685	418.021
n_{Sn}							
0.000421	0.1088	0.0005	10.909	0.007	− 0.185	− 439	324.604
0.000421	0.1963	0.0003	10.750	0.015	− 0.344	− 817	212.632
0.000422	0.2683	0.0002	10.625	0.011	− 0.495	− 1173	88.481
0.000421	0.3283	0.0005	10.661	0.013	− 0.433	− 1029	− 3.182
0.000842	0.4229	0.0004	21.726	0.014	− 0.462	− 549	− 80.032
0.001685	0.5499	0.0001	43.514	0.015	− 0.887	− 526	− 178.162
0.001685	0.6310	0.0002	43.820	0.013	− 0.581	− 345	− 208.239
0.001685	0.6874	0.0004	44.210	0.012	− 0.191	− 113	− 193.786
0.001684	0.7288	0.0006	44.195	0.004	− 0.180	− 107	− 182.231
0.001685	0.7605	0.0003	44.291	0.002	− 0.110	− 65	− 168.539
0.001685	0.7856	0.0005	44.323	0.013	− 0.078	− 46	− 155.718
0.001685	0.8060	0.0003	44.320	0.014	− 0.081	− 48	− 145.551
0.001684	0.8228	0.0002	44.043	0.007	− 0.332	− 197	− 149.986
0.001685	0.8369	0.0005	44.547	0.015	0.146	87	− 131.131
0.001685	0.8489	0.0004	44.554	0.007	0.153	91	− 114.768
0.001685	0.8593	0.0001	44.110	0.015	− 0.291	− 173	− 118.736
0.001685	0.8684	0.0002	44.681	0.011	0.280	166	− 100.397
0.001684	0.8763	0.0004	44.337	0.013	− 0.038	− 23	− 95.701

Table II (continued)

Added moles	Mole fraction (x_{Sn})	Standard uncertainties u(x_{Sn})	Heat effect $H_{signal}{\cdot}K$ (J)	Standard uncertainties $u(\Delta H_{signal}{\cdot}K)$ (J)	Heat of reaction $\Delta H_{reaction}$ (J)	Partial enthalpy $\Delta\overline{H}_{X,i}$ (J mol^{-1})	Integral enthalpy $\Delta \boldsymbol{H}_{\mathbf{mix}}$ (J mol^{-1})
0.001685	0.8834	0.0006	44.136	0.014	− 0.265	− 157	− 99.222
0.001685	0.8897	0.0003	44.710	0.015	0.309	183	− 83.991
Series 3: $(Sb_{0.25}Bi_{0.75})_{1-x}Sn_x$ alloys; atmosphere: argon at pressure $p = 0.1$ MPa; starting amount $n_{Bi} = 0.002586$ mol, $K = 0.002037$ JμVs^{-1}, $T_D = 298$ K, $T_M = 1023$ K, $\Delta H_{Sn}^{T_D \to T_M} = 27340$ (J mol^{-1}), $\Delta H_{Sb}^{T_D \to T_M} = 40228.313$ (J mol^{-1})							
n_{Sb}							
0.000854	0	0.0002	35.807	0.014	1.452	1700	422.021
n_{Sn}							
0.000489	0.1245	0.0009	13.114	0.008	− 0.255	− 521	304.744
0.000424	0.2097	0.0003	11.267	0.012	− 0.325	− 767	200.295
0.000362	0.2704	0.0002	9.448	0.011	− 0.449	− 1240	89.633
0.000382	0.3251	0.0005	10.030	0.012	− 0.414	− 1084	1.702
0.000910	0.4273	0.0004	24.383	0.014	− 0.496	− 545	− 81.132
0.001520	0.5430	0.0001	40.705	0.015	− 0.852	− 561	− 177.867
0.001473	0.6178	0.0002	39.712	0.013	− 0.560	− 380	− 211.044
0.001569	0.6745	0.0004	42.700	0.012	− 0.196	− 125	− 198.251
0.001479	0.7145	0.0007	40.258	0.004	− 0.178	− 120	− 188.636
0.001461	0.7454	0.0003	39.842	0.002	− 0.102	− 70	− 175.835
0.001649	0.7731	0.0004	44.997	0.011	− 0.087	− 53	− 162.390
0.001588	0.7946	0.0003	43.324	0.014	− 0.092	− 58	− 152.526
0.001495	0.8114	0.0002	40.554	0.007	− 0.319	− 213	− 157.524
0.001546	0.8261	0.0004	42.396	0.011	0.128	83	− 138.748
0.001717	0.8400	0.0004	47.097	0.007	0.154	90	− 120.479
0.001572	0.8509	0.0001	42.687	0.015	− 0.291	− 185	− 124.897
0.001592	0.8605	0.0002	43.794	0.011	0.269	169	− 105.944
0.001673	0.8694	0.0004	45.762	0.013	0.022	13	− 98.374
0.001664	0.8772	0.0006	45.163	0.014	− 0.331	− 199	− 104.325
0.002733	0.8881	0.0003	75.013	0.015	0.293	107	− 85.531
0.002338	0.8960	0.0005	63.965	0.013	0.044	19	− 78.168
Series 4: $(Sb_{0.50}Bi_{0.50})_{1-x}Sn_x$ alloys; atmosphere: argon at pressure $p = 0.1$ MPa; starting amount $n_{Bi} = 0.001804$ mol, $K = 0.001986$ JμVs^{-1}, $T_D = 298$ K, $T_M = 923$ K, $\Delta H_{Sn}^{T_D \to T_M} = 24115$ (J mol^{-1}), $\Delta H_{Sb}^{T_D \to T_M} = 37089.563$ (J mol^{-1})							
n_{Sb}							
0.001808	0	0.0003	69.072	0.015	2.014	1114	557.499
n_{Sn}							
0.000510	0.1237	0.0004	10.665	0.005	− 1.634	− 3204	92.212
0.000401	0.2014	0.0003	8.718	0.012	− 0.952	− 2374	− 126.503
0.000563	0.2898	0.0002	12.371	0.011	− 1.206	− 2142	− 349.553
0.000331	0.3332	0.0005	7.168	0.013	− 0.814	− 2459	− 478.446
0.000912	0.4293	0.0007	20.702	0.011	− 1.291	− 1416	− 613.483
0.000898	0.5002	0.0001	20.770	0.015	− 0.885	− 986	− 659.743
0.000897	0.5554	0.0002	20.998	0.012	− 0.633	− 706	− 664.837
0.001006	0.6044	0.0006	23.979	0.015	− 0.281	− 279	− 622.341
0.000994	0.6432	0.0005	23.375	0.007	− 0.595	− 599	− 619.996
0.001537	0.6902	0.0003	36.678	0.002	− 0.387	− 252	− 571.493
0.001485	0.7252	0.0005	35.561	0.013	− 0.250	− 168	− 525.914
0.001522	0.7537	0.0004	36.232	0.016	− 0.471	− 309	− 503.477
0.001641	0.7785	0.0002	39.736	0.007	0.163	99	− 442.832
0.001817	0.8007	0.0005	44.269	0.015	0.452	249	− 373.513
0.001500	0.8160	0.0004	35.570	0.007	− 0.603	− 402	− 375.666

Table II (continued)

Added moles	Mole fraction (x_{Sn})	Standard uncertainties u(x_{Sn})	Heat effect $H_{signal}{\cdot}K$ (J)	Standard uncertainties $u(\Delta H_{signal}{\cdot}K)$ (J)	Heat of reaction $\Delta H_{reaction}$ (J)	Partial enthalpy $\Delta\overline{H}_{X,i}$ (J mol^{-1})	Integral enthalpy $\Delta \boldsymbol{H}_{\mathbf{mix}}$ (J mol^{-1})
0.001584	0.8297	0.0001	38.582	0.015	0.384	242	− 329.526
0.001699	0.8423	0.0002	39.593	0.011	− 1.378	− 811	− 365.215
0.001694	0.8532	0.0004	41.740	0.013	0.889	525	− 303.940
0.001683	0.8626	0.0006	40.568	0.014	− 0.018	− 11	− 285.158
0.001711	0.8710	0.0003	41.248	0.015	− 0.013	− 8	− 268.197
0.001689	0.8783	0.0005	40.697	0.013	− 0.033	− 20	− 254.054
0.001803	0.8853	0.0003	43.504	0.012	0.025	14	− 238.706
0.001740	0.8913	0.0002	41.990	0.004	0.030	17	− 225.330
Series 5: $(Sb_{0.50}Bi_{0.50})_{1-x}Sn_x$ alloys; atmosphere: argon at pressure $p = 0.1$ MPa; starting amount $n_{Sb} = 0.001795$ mol, $K = 0.001984$ JμVs^{-1}, $T_D = 298$ K, $T_M = 973$ K, $\Delta H_{Sn}^{T_D \rightarrow T_M}$ =26351 (J mol^{-1}), $\Delta H_{Bi}^{T_D \rightarrow T_M} = 31240.188$ (J mol^{-1})							
n_{Bi}							
0.001776	0	0.0002	57.491	0.013	2.008	1131	562.233
n_{Sn}							
0.000430	0.1075	0.0008	9.865	0.007	− 1.466	− 3409	135.552
0.000464	0.2002	0.0003	11.108	0.012	− 1.119	− 2412	− 129.272
0.000450	0.2734	0.0004	10.847	0.013	− 1.011	− 2247	− 323.049
0.000439	0.3330	0.0005	10.542	0.014	− 1.026	− 2337	− 488.278
0.000913	0.4302	0.0004	22.755	0.014	− 1.303	− 1427	− 624.997
0.001127	0.5170	0.0001	28.604	0.015	− 1.094	− 971	− 677.689
0.000902	0.5696	0.0001	23.177	0.011	− 0.592	− 656	− 675.395
0.001098	0.6199	0.0004	28.659	0.012	− 0.274	− 250	− 625.561
0.000711	0.6466	0.0006	18.285	0.004	− 0.451	− 634	− 626.263
0.001340	0.6880	0.0003	34.993	0.002	− 0.317	− 237	− 580.567
0.001438	0.7228	0.0004	37.650	0.015	− 0.243	− 169	− 534.680
0.001386	0.7497	0.0003	36.066	0.014	− 0.456	− 329	− 514.657
0.001467	0.7731	0.0002	38.843	0.007	0.186	127	− 454.885
0.001681	0.7950	0.0005	44.750	0.015	0.454	270	− 384.907
0.001678	0.8130	0.0003	43.586	0.005	− 0.631	− 376	− 384.112
0.001896	0.8299	0.0001	50.328	0.015	0.367	194	− 331.932
0.001695	0.8426	0.0002	43.241	0.011	− 1.424	− 840	− 369.935
0.001872	0.8546	0.0003	50.244	0.012	0.915	489	− 304.458
0.001875	0.8649	0.0006	49.386	0.017	− 0.022	− 12	− 283.694
0.001769	0.8734	0.0003	46.581	0.015	− 0.034	− 19	− 267.106
0.001971	0.8816	0.0004	51.914	0.016	− 0.024	− 12	− 250.468
0.001819	0.8884	0.0003	47.961	0.012	0.029	16	− 235.309
Series 6: $(Sb_{0.50}Bi_{0.50})_{1-x}Sn_x$ alloys; atmosphere: argon at pressure $p = 0.1$ MPa; starting amount $n_{Sb} = 0.001836$ mol, $K = 0.002004$ JμVs^{-1}, $T_D = 298$ K, $T_M = 1023$ K, $\Delta H_{Sn}^{T_D \rightarrow T_M} = 27340$ (J mol^{-1}), $\Delta H_{Bi}^{T_D \rightarrow T_M} = 32830.488$ (J mol^{-1})							
n_{Bi}							
0.001814	0	0.0004	61.626	0.013	2.071	1142	567.478
n_{Sn}							
0.000452	0.1102	0.0004	10.793	0.005	− 1.565	− 3462	123.469
0.000446	0.1974	0.0003	11.113	0.011	− 1.081	− 2424	− 126.395
0.000398	0.2620	0.0007	9.954	0.015	− 0.927	− 2329	− 303.701
0.000530	0.3335	0.0005	13.271	0.012	− 1.219	− 2300	− 496.972
0.000767	0.4153	0.0004	19.840	0.014	− 1.130	− 1473	− 616.843
0.000920	0.4904	0.0002	24.188	0.015	− 0.965	− 1049	− 672.320
0.001047	0.5554	0.0003	27.846	0.013	− 0.779	− 744	− 681.431
0.001154	0.6102	0.0005	31.210	0.012	− 0.340	− 295	− 633.798

Table II (continued)

Added moles	Mole fraction (x_{Sn})	Standard uncertainties u(x_{Sn})	Heat effect $H_{signal}{\cdot}K$ (J)	Standard uncertainties $u(\Delta H_{signal}{\cdot}K)$ (J)	Heat of reaction $\Delta H_{reaction}$ (J)	Partial enthalpy $\Delta\overline{H}_{X,i}$ (J mol^{-1})	Integral enthalpy $\Delta \boldsymbol{H}_{\mathbf{mix}}$ (J mol^{-1})
0.001053	0.6496	0.0006	28.155	0.004	− 0.634	− 602	− 630.634
0.001416	0.6915	0.0003	38.387	0.002	− 0.326	− 230	− 582.703
0.001499	0.7262	0.0007	40.741	0.014	− 0.242	− 161	− 535.313
0.001646	0.7563	0.0003	44.479	0.014	− 0.523	− 318	− 511.402
0.001737	0.7816	0.0009	47.691	0.007	0.201	116	− 446.221
0.001842	0.8033	0.0005	50.886	0.015	0.526	286	− 373.611
0.001857	0.8212	0.0004	50.075	0.007	− 0.695	− 374	− 373.665
0.001828	0.8359	0.0001	50.418	0.015	0.440	241	− 323.154
0.002001	0.8494	0.0002	53.110	0.011	− 1.597	− 798	− 362.371
0.001794	0.8598	0.0004	50.099	0.013	1.051	586	− 297.046
0.001732	0.8686	0.0006	47.318	0.014	− 0.035	− 20	− 279.782
0.001761	0.8764	0.0003	48.195	0.015	0.049	28	− 261.441
0.001782	0.8834	0.0005	48.696	0.013	− 0.024	− 13	− 247.302
0.001826	0.8899	0.0003	49.954	0.012	0.031	17	− 232.739
Series 7: $(Sb_{0.75}Bi_{0.25})_{1-x}Sn_x$ alloys; atmosphere: argon at pressure $p = 0.1$ MPa; starting amount $n_{Sb} = 0.003269$ mol, $K = 0.001912$ JμVs^{-1}, $T_D = 298$ K, $T_M = 923$ K, $\Delta H_{Sn}^{T_D \to T_M} = 24115$ (J mol^{-1}), $\Delta H_{Bi}^{T_D \to T_M} = 29649.888$ (J mol^{-1})							
n_{Bi}							
0.001084	0	0.0002	33.955	0.011	1.815	1674	417.008
n_{Sn}							
0.000510	0.1049	0.0004	9.684	0.005	− 2.615	− 5127	− 164.573
0.000545	0.1951	0.0006	11.029	0.012	− 2.114	− 3879	− 538.871
0.000476	0.2602	0.0002	9.695	0.014	− 1.784	− 3748	− 798.353
0.000453	0.3131	0.0007	9.639	0.017	− 1.285	− 2837	− 944.150
0.000877	0.3966	0.0004	19.208	0.012	− 1.941	− 2213	− 1098.386
0.001011	0.4708	0.0002	22.780	0.015	− 1.600	− 1583	− 1157.940
0.000585	0.5059	0.0003	13.663	0.013	− 0.444	− 759	− 1131.438
0.000791	0.5466	0.0004	18.041	0.012	− 1.034	− 1307	− 1145.957
0.000976	0.5884	0.0007	22.802	0.005	− 0.734	− 752	− 1109.589
0.000827	0.6183	0.0003	19.458	0.002	− 0.485	− 586	− 1071.649
0.001375	0.6594	0.0005	32.552	0.013	− 0.606	− 441	− 1003.773
0.001546	0.6961	0.0003	37.088	0.014	− 0.194	− 125	− 908.958
0.001635	0.7273	0.0002	38.783	0.007	− 0.645	− 394	− 856.296
0.001683	0.7533	0.0004	40.319	0.013	− 0.267	− 159	− 789.711
0.001694	0.7749	0.0004	40.270	0.007	− 0.581	− 343	− 750.570
0.001854	0.7946	0.0001	44.942	0.015	0.233	126	− 673.909
0.001694	0.8098	0.0002	40.297	0.011	− 0.554	− 327	− 648.254
0.001855	0.8241	0.0004	45.102	0.013	0.369	199	− 584.722
0.001528	0.8343	0.0006	36.796	0.014	− 0.052	− 34	− 552.676
0.001561	0.8436	0.0004	36.755	0.017	− 0.889	− 570	− 553.621
0.001578	0.8520	0.0005	38.851	0.013	0.798	506	− 496.777
0.001808	0.8605	0.0004	43.888	0.010	0.288	159	− 458.789
0.001515	0.8670	0.0002	36.193	0.004	− 0.341	− 225	− 447.970
0.001659	0.8734	0.0005	39.985	0.002	− 0.022	− 13	− 426.994
0.001622	0.8791	0.0004	39.068	0.013	− 0.047	− 29	− 409.079
0.001824	0.8849	0.0001	44.014	0.014	0.028	15	− 388.598
0.001612	0.8896	0.0002	38.819	0.007	− 0.054	− 33	− 374.106

Table II (continued)

Added moles	Mole fraction (x_{Sn})	Standard uncertainties u(x_{Sn})	Heat effect $H_{signal}{\cdot}K$ (J)	Standard uncertainties $u(\Delta H_{signal}{\cdot}K)$ (J)	Heat of reaction $\Delta H_{reaction}$ (J)	Partial enthalpy $\Delta\overline{H}_{X,i}$ (J mol^{-1})	Integral enthalpy $\boldsymbol{\Delta H_{mix}}$ (J mol^{-1})
Series 8: $(Sb_{0.75}Bi_{0.25})_{1-x}Sn_x$ alloys; atmosphere: argon at pressure $p = 0.1$ MPa; starting amount $n_{Sb} = 0.003285$ mol, $K = 0.002048$ JμVs^{-1}, $T_D = 298$ K, $T_M = 973$ K, $\Delta H_{Sn}^{T_D \to T_M}$ =26351 (J mol^{-1}), $\Delta H_{Bi}^{T_D \to T_M} = 31240.19$ (J mol^{-1})							
n_{Bi}							
0.001086	0	0.0004	35.765	0.008	1.838	1692	420.432
n_{Sn}							
0.000417	0.0871	0.0007	8.673	0.009	− 2.315	− 5552	− 99.676
0.000220	0.1272	0.0002	4.770	0.013	− 1.027	− 4668	− 300.249
0.000476	0.2030	0.0003	10.635	0.011	− 1.908	− 4008	− 622.186
0.000546	0.2751	0.0005	12.692	0.015	− 1.696	− 3106	− 847.151
0.000256	0.3046	0.0004	6.153	0.014	− 0.593	− 2316	− 906.882
0.000482	0.3542	0.0001	11.711	0.015	− 0.990	− 2054	− 988.576
0.000503	0.3988	0.0002	12.045	0.013	− 1.210	− 2406	− 1086.704
0.000372	0.4281	0.0007	9.265	0.012	− 0.538	− 1446	− 1104.138
0.001282	0.5103	0.0006	31.935	0.004	− 1.847	− 1441	− 1152.507
0.001059	0.5622	0.0003	26.920	0.002	− 0.986	− 931	− 1129.049
0.001286	0.6122	0.0004	33.023	0.011	− 0.864	− 672	− 1076.825
0.001576	0.6597	0.0003	40.803	0.014	− 0.726	− 461	− 1001.240
0.001832	0.7022	0.0002	47.880	0.007	− 0.395	− 216	− 903.171
0.001552	0.7307	0.0005	40.561	0.015	− 0.336	− 216	− 837.524
0.002336	0.7646	0.0004	60.753	0.007	− 0.803	− 344	− 775.410
0.002959	0.7969	0.0001	77.928	0.015	− 0.045	− 15	− 670.879
0.002403	0.8173	0.0002	62.692	0.011	− 0.629	− 262	− 629.802
0.002589	0.8352	0.0004	68.569	0.013	0.346	134	− 555.256
0.002276	0.8482	0.0006	59.884	0.014	− 0.091	− 40	− 514.545
0.002919	0.8622	0.0003	75.849	0.015	− 1.070	− 367	− 500.907
0.002621	0.8727	0.0005	69.967	0.013	0.901	344	− 436.435
0.002964	0.8828	0.0003	78.434	0.012	0.330	111	− 392.896
0.002608	0.8905	0.0002	68.322	0.004	− 0.401	− 154	− 377.266
Series 9: $(Sb_{0.75}Bi_{0.25})_{1-x}Sn_x$ alloys; atmosphere: argon at pressure $p = 0.1$ MPa; starting amount $n_{Sb} = 0.002900$ mol, $K = 0.002106$ JμVs^{-1}, $T_D = 298$ K, $T_M = 1023$ K, $\Delta H_{Sn}^{T_D \to T_M}$ =27340 (J mol^{-1}), $\Delta H_{Bi}^{T_D \to T_M} = 32830.488$ (J mol^{-1})							
n_{Bi}							
0.000967	0	0.0005	33.387	0.012	1.640	1696	424.125
n_{Sn}							
0.000417	0.0973	0.0004	9.129	0.006	− 2.272	− 5448	− 147.426
0.000476	0.1876	0.0003	11.133	0.015	− 1.881	− 3952	− 527.943
0.000280	0.2327	0.0005	6.473	0.011	− 1.182	− 4221	− 733.064
0.000376	0.2860	0.0006	9.144	0.011	− 1.136	− 3021	− 892.074
0.001121	0.4084	0.0007	28.065	0.014	− 2.583	− 2304	− 1134.091
0.000732	0.4680	0.0001	19.113	0.014	− 0.900	− 1230	− 1143.729
0.001687	0.5682	0.0002	44.392	0.013	− 1.731	− 1026	− 1121.625
0.001544	0.6317	0.0004	41.273	0.011	− 0.940	− 609	− 1046.173
0.002283	0.6975	0.0008	61.599	0.004	− 0.818	− 358	− 923.373
0.001701	0.7330	0.0003	46.142	0.002	− 0.363	− 213	− 839.946
0.001611	0.7597	0.0007	43.804	0.011	− 0.241	− 150	− 770.874
0.002045	0.7868	0.0003	55.700	0.014	− 0.210	− 103	− 695.527
0.001021	0.7982	0.0002	27.844	0.007	− 0.070	− 69	− 662.103
0.002908	0.8248	0.0005	79.347	0.012	− 0.158	− 54	− 582.028
0.001459	0.8356	0.0004	38.644	0.007	− 1.245	− 853	− 598.863

Table II (continued)

Added moles	Mole fraction (x_{Sn})	Standard uncertainties u(x_{Sn})	Heat effect $H_{signal}{\cdot}K$ (J)	Standard uncertainties $u(\Delta H_{signal}{\cdot}K)$ (J)	Heat of reaction $\Delta H_{reaction}$ (J)	Partial enthalpy $\Delta\overline{H}_{X,i}$ (J mol^{-1})	Integral enthalpy $\boldsymbol{\Delta H_{mix}}$ (J mol^{-1})
0.001532	0.8457	0.0001	42.460	0.014	0.575	375	− 539.319
0.002215	0.8582	0.0002	59.954	0.011	− 0.604	− 273	− 517.646
0.002894	0.8718	0.0008	79.666	0.013	0.544	188	− 449.970
0.001568	0.8782	0.0006	42.890	0.014	0.021	13	− 427.060
0.001656	0.8842	0.0003	44.239	0.015	− 1.036	− 626	− 436.904
0.002472	0.8922	0.0005	68.630	0.013	1.046	423	− 377.645

[a]Standard uncertainties u are: $u(T_M)$ = 0.1 K, $u(p)$ = 11 kPa, $u(n_{Bi})$ = 0.000001 mol, $u(n_{Sn})$ = 0.000001 mol, $u(n_{Sb})$ = 0.000002 mol, $u(\Delta H_{reaction})$ = 0.001 J; Series 1:$u(K)$ = 0.000003 J/μV s, $u(\Delta_{mix}H)$ = 20.0213 J mol^{-1}; Series 2: $u(K)$ = 0.000002 J/μV s, $u(\Delta_{mix}H)$ = 18.017 Jmol^{-1}, Series 3: $u(K)$ = 0.000002 J/μV s, $u(\Delta_{mix}H)$ = 21.018 Jmol^{-1}; Series 4: $u(K)$ = 0.000004 J/μV s, $u(\Delta_{mix}H)$ = 45.017 J mol^{-1}; Series 5: $u(K)$ = 0.000001 J/μV s, $u(\Delta_{mix}H)$ = 43.014 J mol^{-1}; Series 6: $u(K)$ = 0. 000001 J/μV s, $u(\Delta_{mix}H)$ = 46.017 J mol^{-1}; Series 7: $u(K)$ = 0. 000001 J/μV s, $u(\Delta_{mix}H)$ = 75.012 J mol^{-1}; Series 8: $u(K)$ = 0. 000004 J/μV s, $u(\Delta_{mix}H)$ = 78.025 J mol^{-1}; Series 9: $u(K)$ = 0. 000003 J/μV s, $u(\Delta_{mix}H)$ = 80.007 J mol^{-1}

[b]T_D = drop temperature in Kelvin, T_M = bath temperature in Kelvin, n_{sn} = number of moles of tin, n_{Bi} = number of moles of bismuth, n_{sb} = number of moles of antimony, K = calibration constant, ΔH_{Signal} = the heat effect due to single drop of sample to the bath, $\Delta_{mix}H$ = integral enthalpy of mixing of Sn-Bi-Sb system

923 K, 973 K, and 1023 K are quite close to each other. This makes the mixing enthalpy of Sn-Bi-Sb system's independent of temperature. Temperature has very little effect on how the Bi, Sn, and Sb atoms in this system interact with one another in the above temperature range. The degree of mixing is better when the curve is more symmetric. In the temperature range of 923–1023 K, the $(Sb_{0.75}Bi_{0.25})_{1-x}Sn_x$ alloy mixes better than the other two alloys.

Figure 6 illustrates the nature of mixing enthalpies with the variations in the composition of Bi. In the given cross-section, the mixing enthalpy maxima are endothermic in nature. The asymmetrical nature of the enthalpy of mixing curve and the large value of the enthalpy of mixing makes the alloy less stable. The amount of heat needed to produce these alloys would depend on their composition. The enthalpy of mixing rises with Bi concentration, reaching a peak around x_{Bi} ~ 0.72.

Figure 7 further shows the enthalpies of mixing plots for a given ternary system at 923 K, 973 K, and 1023 K as a function of composition. These plots are quite close to each other. This might mean that, in the Sn-Bi-Sb system, mixing enthalpy is almost independent of temperature and mixing behavior does not significantly alter with the variation of temperature.

Figure 8 illustrates the relationship between mixing enthalpies with variation in Sb composition of the given ternary alloy system. In the given cross-section, the minima of the mixing enthalpy is exothermic in nature which makes the alloy more stable. In the cross-section $(Bi_{0.50}Sn_{0.50})_{1-x}Sb_x$, the minima of enthalpy of mixing is almost symmetric with regard to antimony composition.

The enthalpy of mixing falls as antimony concentration rises, reaching minima at x_{Sb} ~ 0.50. It reaches its peak at equi-atomic percent and then decreases at the end.

The Bi, Sb, and Sn atoms' interatomic attraction may have diminished as a result. Regardless of the mixing entropy's sign, the mixing enthalpy adds adversely to the Gibbs energy for the majority of the Sn composition. The measured mixing enthalpy was found to be negative, which suggests that the atoms in this system have finite amounts of interatomic interaction energy. Therefore, heat produced by the mixing process is exothermic and is released during the mixing process.

Figure 9 further shows that the plots at 923 K, 973 K, and 1023 K are quite near to each other. This suggests that the Sn-Bi-Sb system's enthalpy of mixing is nearly temperature-independent.

The plots between molar enthalpy of mixing and the composition of dropping species was used to create the above curves. It is shown in Fig. 10 for nine iso-enthalpies, i.e., 0.2 kJ/mol, 0.4 kJ/mol, − 0.2 kJ/mol, − 0.4 kJ/mol, − 0.6 kJ/mol, − 0.8 kJ/mol, − 1.0 kJ/mol, − 1.2 kJ/mol, and − 1.4 kJ/mol. The mixing enthalpy is seen to be more negative when the alloy's composition is nearer to the Sb-Sn binary system and positive when it is nearer to the Bi-Sb binary system. This is because the Sb-Sn binary system has the largest negative mixing enthalpy values among the three binaries, whereas the Bi-Sb alloys have the highest positive enthalpy of mixing values. The binary Sb-Sn affects the majority of the iso-enthalpy curves. This suggests that the Sb and Sn atoms in the given ternary systems' sub-lattices may have a greater influence on the orientation of the enthalpy of mixing curves.

Table III Partial and integral mixing enthalpies of Sn-Bi-Sb alloys when Bi dropped

Added moles	Mole fraction (x_{Bi})	Standard uncertainties u (x_{Bi})	Heat effect $H_{Signal} \cdot K$ (J)	Standard uncertainties u($\Delta H_{Signal} \cdot K$) (J)	Heat of reaction $\Delta H_{Reaction}$ (J)	Partial enthalpy $\Delta\overline{H}_{X,i}$(J mol^{-1})	Integral enthalpy $\Delta H_{\mathbf{mix}}$ (J mol^{-1})
Series 1: $(Sb_{0.50}Sn_{0.50})_{1-x}Bi_x$ alloys; atmosphere: argon at pressure $p = 0.1$ MPa; starting amount $n_{Sb} = 0.001191$ mol, $K = 0.001986$ JμVs^{-1}, $T_D = 298$ K, $T_M = 923$ K, $\Delta H_{Sn}^{T_D \to T_M} = 24115$ (J mol^{-1}), $\Delta H_{Bi}^{T_D \to T_M} = 29649.888$ (J mol^{-1})							
n_{Sn}							
0.001179	0	0.0002	25.060	0.013	− 3.372	− 2860	− 1422.75
n_{Bi}							
0.000290	0.1090	0.0005	8.706	0.004	0.108	372	− 1226.939
0.000228	0.1794	0.0003	7.150	0.012	0.390	1711	− 995.116
0.000319	0.2610	0.0005	9.987	0.011	0.529	1658	− 731.181
0.000331	0.3301	0.0004	10.509	0.013	0.695	2100	− 466.359
0.000517	0.4155	0.0004	16.136	0.017	0.807	1561	− 208.002
0.000510	0.4808	0.0001	15.832	0.015	0.711	1394	− 28.980
0.000510	0.5330	0.0002	15.692	0.016	0.571	1120	86.473
0.000572	0.5803	0.0003	17.522	0.015	0.562	983	177.282
0.000564	0.6184	0.0006	17.059	0.004	0.336	596	215.188
0.000873	0.6654	0.0004	26.337	0.005	0.453	519	252.709
0.000844	0.7011	0.0005	25.341	0.013	0.316	374	265.665
0.000864	0.7304	0.0003	26.121	0.014	0.503	582	296.716
0.000933	0.7563	0.0002	27.591	0.007	− 0.072	− 77	260.837
0.001031	0.7797	0.0008	30.724	0.012	0.155	150	250.292
0.000853	0.7958	0.0004	25.389	0.007	0.098	115	240.369
0.000900	0.8105	0.0001	26.892	0.015	0.207	230	239.572
0.000964	0.8241	0.0004	28.526	0.012	− 0.056	− 58	218.267
0.000963	0.8358	0.0004	28.607	0.013	0.054	56	207.434
0.000956	0.8460	0.0006	28.388	0.014	0.043	45	197.362
0.000972	0.8552	0.0003	29.182	0.015	0.362	372	207.779
0.000960	0.8632	0.0005	28.163	0.013	− 0.301	− 314	178.876
0.001024	0.8708	0.0003	30.386	0.012	0.025	24	170.253
0.000988	0.8774	0.0002	28.926	0.004	− 0.368	− 372	142.556
0.001441	0.8859	0.0005	43.345	0.002	0.620	430	162.509
Series 2: $(Sb_{0.50}Sn_{0.50})_{1-x}Bi_x$ alloys: atmosphere: argon at pressure $p = 0.1$ MPa; starting amount $n_{Sb} = 0.001191$ mol, $K = 0.001984$ JμVs^{-1}, $T_D = 298$ K, $T_M = 973$ K, $\Delta H_{Sn}^{T_D \to T_M} = 26351$ (J mol^{-1}), $\Delta H_{Bi}^{T_D \to T_M} = 31240.188$ (J mol^{-1})							
n_{Sn}							
0.001179	0	0.0003	27.682	0.011	− 3.386	− 2872	− 1428.779
n_{Bi}							
0.000244	0.0933	0.0004	7.621	0.007	− 0.002	− 8	− 1295.942
0.000151	0.1429	0.0003	4.986	0.012	0.269	1781	− 1128.080
0.000369	0.2438	0.0002	12.170	0.011	0.642	1740	− 790.230
0.000071	0.2605	0.0007	2.396	0.015	0.178	2507	− 717.174
0.000332	0.3299	0.0004	11.001	0.014	0.629	1895	− 472.155
0.000640	0.4326	0.0004	21.052	0.017	1.058	1653	− 146.463
0.000513	0.4947	0.0002	16.700	0.013	0.674	1314	13.120
0.000623	0.5539	0.0007	20.225	0.012	0.762	1223	155.011
0.000664	0.6035	0.0006	21.166	0.003	0.423	637	208.551
0.000502	0.6342	0.0004	15.993	0.002	0.310	618	240.311
0.000816	0.6751	0.0005	25.845	0.013	0.353	433	261.756
0.000788	0.7068	0.0002	25.122	0.014	0.505	641	298.738
0.000833	0.7342	0.0007	25.967	0.007	− 0.056	− 67	264.563
0.000955	0.7599	0.0005	30.006	0.012	0.172	180	256.424

Table III (continued)

Added moles	Mole fraction (x_{Bi})	Standard uncertainties u (x_{Bi})	Heat effect $H_{Signal} \cdot K$ (J)	Standard uncertainties u($\Delta H_{Signal} \cdot K$) (J)	Heat of reaction $\Delta H_{Reaction}$ (J)	Partial enthalpy $\Delta\overline{H}_{X,i}$(J mol^{-1})	Integral enthalpy ΔH_{mix} (J mol^{-1})
0.000953	0.7810	0.0004	29.916	0.007	0.144	151	247.155
0.001077	0.8009	0.0001	33.906	0.015	0.260	241	246.588
0.000963	0.8158	0.0002	30.039	0.011	− 0.045	− 47	224.665
0.001064	0.8298	0.0004	33.318	0.013	0.078	73	213.104
0.001065	0.8419	0.0006	33.334	0.014	0.063	59	202.138
0.001004	0.8518	0.0003	31.745	0.015	0.380	378	213.219
0.001120	0.8615	0.0005	34.700	0.013	− 0.289	− 258	182.363
0.001033	0.8694	0.0003	32.295	0.012	0.024	23	173.345
0.001493	0.8793	0.0002	46.291	0.004	− 0.351	− 235	142.266
Series 3: $(Sb_{0.50}Sn_{0.50})_{1-x}Bi_x$ alloys; atmosphere: argon at pressure $p = 0.1$ MPa; starting amount $n_{Sb} = 0.001191$ mol, $K = 0.002004$ JμVs^{-1}, $T_D = 298$ K, $T_M = 1023$ K, $\Delta H_{Sn}^{T_D \to T_M}$ =27340 (J mol^{-1}), $\Delta H_{Bi}^{T_D \to T_M} = 32830.488$ (J mol^{-1})							
n_{Sn}							
0.001179	0	0.0004	28.834	0.011	− 3.400	− 2884	− 1434.779
n_{Bi}							
0.000257	0.0978	0.0005	8.445	0.007	0.008	31	− 1291.193
0.000253	0.1771	0.0007	8.741	0.015	0.435	1719	− 1026.568
0.000226	0.2370	0.0002	7.828	0.011	0.408	1805	− 820.816
0.000177	0.2781	0.0006	6.358	0.012	0.547	3090	− 609.656
0.000144	0.3084	0.0004	5.201	0.014	0.473	3285	− 446.165
0.000522	0.3998	0.0001	18.003	0.015	0.865	1657	− 168.126
0.000595	0.4784	0.0007	20.277	0.013	0.743	1249	17.456
0.000655	0.5441	0.0004	22.199	0.017	0.695	1061	148.836
0.000599	0.5912	0.0006	20.069	0.004	0.404	674	203.211
0.000804	0.6410	0.0003	26.871	0.002	0.475	591	250.343
0.000852	0.6820	0.0005	28.333	0.016	0.361	424	270.189
0.000934	0.7175	0.0008	31.235	0.014	0.571	611	308.122
0.000987	0.7472	0.0002	32.354	0.007	− 0.050	− 51	270.441
0.001046	0.7726	0.0005	34.517	0.015	0.176	168	260.135
0.001056	0.7935	0.0004	34.818	0.007	0.149	141	249.208
0.001038	0.8106	0.0009	34.324	0.015	0.246	237	248.205
0.001136	0.8264	0.0002	37.250	0.011	− 0.045	− 40	224.238
0.001020	0.8385	0.0004	33.545	0.013	0.058	57	212.616
0.000983	0.8486	0.0006	32.313	0.014	0.041	42	201.843
0.001001	0.8577	0.0003	33.261	0.015	0.398	398	213.622
0.001012	0.8659	0.0005	32.885	0.013	− 0.339	− 335	182.221
0.001037	0.8733	0.0003	34.066	0.012	0.021	20	173.210

[a]Standard uncertainties u are: $u(T_M) = 0.1$ K, $u(p) = 12$ kPa, $u(n_{Bi}) = 0.000002$ mol, $u(n_{Sn}) = 0.000001$ mol, $u(n_{Sb}) = 0.000002$ mol, $u(\Delta H_{reaction}) = 0.001$ J; Series 1:$u(K) = 0.000002$ J/μV s, $u(\Delta_{mix}H) = 70.013$ J mol^{-1}; Series 2: $u(K) = 0.000002$ J/μV s, $u(\Delta_{mix}H) = 72.017$ Jmol^{-1}, Series 3: $u(K) = 0.000003$ J/μV s, $u(\Delta_{mix}H) = 75.018$ Jmol^{-1}.

[b]T_D = drop temperature in Kelvin, T_M = bath temperature in Kelvin, n_{sn} = number of moles of tin, n_{Bi} = number of moles of bismuth, n_{sb} = number of moles of antimony, K = calibration constant, ΔH_{Signal} = the heat effect due to a single drop of sample to the bath, $\Delta_{mix}H$ = integral enthalpy of mixing of Sn-Bi-Sb system

The thermodynamic characteristics of various type of systems may be ternary or a higher order may be deduced from the data of different binaries using a variety of theoretical models. The theoretical model put forward by Ansara and Dupin is significant.[42] The RKM polynomial has also been employed by Luef et al.[43] for substitutional solutions. We have used the least squares fitting for the given dataset as in:

Table IV Partial and integral mixing enthalpies of Sn-Bi-Sb alloys when Sb dropped

Added moles	Mole fraction (x_{Sb})	Standard uncertainties $u(x_{Sb})$	Heat effect $H_{Signal} \cdot K$ (J)	Standard uncertainties u($\Delta H_{Signal} \cdot K$) (J)	Heat of reaction $\Delta H_{reaction}$ (J)	Partial enthalpy $\Delta \overline{H}_{X,i}$ (J mol^{-1})	Integral enthalpy ΔH_{mix} (J mol^{-1})
Series 1: $(Bi_{0.50}Sn_{0.50})_{1-x}Sb_x$ alloys; atmosphere: argon at pressure $p = 0.1$ MPa; starting amount $n_{Sn} = 0.001855$ mol, $K = 0.001986$ JμVs^{-1}, $T_D = 298$ K, $T_M = 923$ K, $\Delta H_{Sb}^{T_D \rightarrow T_M} = 37089.563$ (J mol^{-1}), $\Delta H_{Bi}^{T_D \rightarrow T_M} = 29649.888$ (J mol^{-1})							
n_{Bi}							
0.001804	0	0.0004	53.947	0.005	0.459	254.00	125.324
n_{Sb}							
0.000497	0.1196	0.0005	17.733	0.007	− 0.701	− 1410	− 58.118
0.000392	0.1955	0.0007	13.779	0.013	− 0.760	− 1939	− 220.361
0.000548	0.2820	0.0002	19.284	0.011	− 1.041	− 1900	− 400.994
0.000394	0.3335	0.0004	14.063	0.016	− 0.550	− 1396	− 472.399
0.000889	0.4264	0.0004	31.697	0.014	− 1.276	− 1435	− 606.449
0.000876	0.4957	0.0001	31.717	0.015	− 0.773	− 882	− 639.770
0.000874	0.5499	0.0003	32.239	0.017	− 0.177	− 203	− 592.790
0.000982	0.5984	0.0004	35.752	0.012	− 0.670	− 682	− 602.423
0.000968	0.6370	0.0006	35.716	0.004	− 0.187	− 193	− 563.155
0.001499	0.6840	0.0007	55.716	0.003	0.119	79	− 479.969
0.001448	0.7191	0.0005	53.488	0.013	− 0.218	− 151	− 443.361
0.001483	0.7478	0.0003	55.079	0.014	0.075	51	− 392.889
0.001601	0.7729	0.0002	59.509	0.007	0.129	81	− 345.837
0.00177	0.7954	0.0005	65.804	0.015	0.155	88	− 302.931
0.001463	0.8108	0.0004	54.779	0.007	0.517	353	− 253.268
0.001545	0.8248	0.0001	57.056	0.015	− 0.247	− 160	− 246.384
0.001656	0.8377	0.0002	61.559	0.011	0.139	84	− 222.083
0.001651	0.8488	0.0004	61.374	0.013	0.139	84	− 201.213
0.001641	0.8584	0.0006	60.992	0.014	0.128	78	− 183.480
0.001669	0.8670	0.0003	62.031	0.015	0.129	77	− 167.658
0.001647	0.8745	0.0005	61.200	0.013	0.113	69	− 154.308
0.001757	0.8816	0.0003	65.278	0.012	0.112	64	− 141.890
0.001696	0.8878	0.0002	63.000	0.004	0.096	57	− 131.574
Series 2: $(Bi_{0.50}Sn_{0.50})_{1-x}Sb_x$ alloys; atmosphere: argon at pressure $p = 0.1$ MPa; starting amount $n_{Sn} = 0.001855$ mol, $K = 0.001984$ JμVs^{-1}, $T_D = 298$ K, $T_M = 973$ K, $\Delta H_{Sb}^{T_D \rightarrow T_M} = 38658.938$ (J mol^{-1}), $\Delta H_{Bi}^{T_D \rightarrow T_M} = 31240.188$ (J mol^{-1})							
n_{Bi}							
0.001804	0	0.0006	56.827	0.015	0.470	261	128.324
n_{Sb}							
0.000591	0.1391	0.0005	22.005	0.008	− 0.842	− 1425	− 87.534
0.000280	0.1923	0.0004	10.215	0.015	− 0.610	− 2179	− 216.834
0.00044	0.2638	0.0002	16.060	0.013	− 0.950	− 2159	− 388.699
0.000121	0.2813	0.0007	4.630	0.017	− 0.048	− 397	− 388.833
0.000395	0.3330	0.0004	14.633	0.014	− 0.637	− 1613	− 476.945
0.001098	0.4443	0.0007	41.120	0.016	− 1.328	− 1209	− 599.142
0.00088	0.5098	0.0002	33.345	0.013	− 0.675	− 767	− 618.919
0.00107	0.5712	0.0006	40.602	0.012	− 0.763	− 713	− 630.771
0.000693	0.6034	0.0007	26.652	0.004	− 0.139	− 201	− 598.484
0.001307	0.6526	0.0003	50.615	0.002	0.088	67	− 515.849
0.001402	0.6934	0.0005	53.945	0.013	− 0.255	− 182	− 476.607
0.001352	0.7246	0.0007	52.329	0.014	0.062	46	− 423.485
0.00143	0.7514	0.0002	55.395	0.007	0.113	79	− 374.636
0.001639	0.7763	0.0005	63.500	0.015	0.138	84	− 328.685
0.001636	0.7966	0.0004	63.721	0.007	0.475	290	− 272.382

Table IV (continued)

Added moles	Mole fraction (x_{Sb})	Standard uncertainties $u(x_{Sb})$	Heat effect $H_{Signal} \cdot K$ (J)	Standard uncertainties u($\Delta H_{Signal} \cdot K$) (J)	Heat of reaction $\Delta H_{reaction}$ (J)	Partial enthalpy $\Delta\overline{H}_{X,i}$ (J mol^{-1})	Integral enthalpy ΔH_{mix} (J mol^{-1})
0.001848	0.8156	0.0001	71.164	0.015	− 0.278	− 150	− 261.028
0.001652	0.8298	0.0002	64.003	0.011	0.138	84	− 234.552
0.001826	0.8431	0.0004	70.719	0.013	0.128	70	− 210.684
0.001828	0.8545	0.0006	70.775	0.014	0.106	58	− 191.159
0.001724	0.8638	0.0003	66.774	0.015	0.126	73	− 174.200
0.001922	0.8729	0.0005	74.409	0.013	0.107	56	− 158.869
0.001774	0.8803	0.0003	68.688	0.012	0.107	60	− 146.148
Series 3: $(Bi_{0.50}Sn_{0.50})_{1-x}Sb_x$ alloys; atmosphere: argon at pressure $p = 0.1$ MPa; starting amount $n_{Sn} = 0.001855$ mol, $K = 0.002004$ JμVs^{-1}, $T_D = 298$ K, $T_M = 1023$ K, $\Delta H_{Sb}^{T_D \to T_M} = 40228.313$ (J mol^{-1}), $\Delta H_{Bi}^{T_D \to T_M} = 32830.488$ (J mol^{-1})							
n_{Bi}							
0.001804	0	0.0004	59.710	0.015	0.484	268	132.325
n_{Sb}							
0.000441	0.1076	0.0005	17.115	0.007	− 0.626	− 1420	− 34.595
0.000434	0.1930	0.0003	16.611	0.013	− 0.848	− 1954	− 218.376
0.000388	0.2566	0.0007	14.746	0.011	− 0.863	− 2224	− 376.474
0.000304	0.2998	0.0005	11.829	0.014	− 0.400	− 1316	− 431.209
0.000246	0.3313	0.0003	9.553	0.017	− 0.343	− 1394	− 474.417
0.000897	0.4255	0.0001	34.947	0.015	− 1.138	− 1269	− 586.267
0.001021	0.5049	0.0004	40.233	0.011	− 0.840	− 823	− 618.921
0.001125	0.5703	0.0005	44.712	0.012	− 0.545	− 484	− 601.203
0.001027	0.6165	0.0006	41.041	0.004	− 0.273	− 266	− 565.056
0.00138	0.6650	0.0007	55.350	0.002	− 0.165	− 120	− 508.804
0.001462	0.7045	0.0005	58.781	0.013	− 0.033	− 23	− 451.354
0.001604	0.7384	0.0008	64.251	0.014	− 0.275	− 171	− 419.307
0.001694	0.7667	0.0002	68.245	0.007	0.098	58	− 367.778
0.001796	0.7907	0.0005	72.404	0.015	0.154	86	− 321.159
0.001811	0.8103	0.0007	73.373	0.007	0.520	287	− 264.045
0.001782	0.8263	0.0001	71.394	0.015	− 0.293	− 164	− 255.603
0.001951	0.8411	0.0002	78.616	0.011	0.131	67	− 228.249
0.001749	0.8523	0.0004	70.500	0.013	0.141	81	− 206.432
0.001689	0.8617	0.0006	68.089	0.014	0.143	85	− 187.878
0.001716	0.8701	0.0003	69.164	0.015	0.132	77	− 171.729
0.001738	0.8777	0.0005	70.036	0.013	0.119	68	− 157.773
0.00178	0.8846	0.0003	71.731	0.012	0.125	70	− 144.984

[a]Standard uncertainties u are: $u(T_M) = 0.1$ K, $u(p) = 10$ kPa, $u(n_{Bi}) = 0.000003$ mol, $u(n_{Sn}) = 0.000002$ mol, $u(n_{Sb}) = 0.000005$ mol, $u(\Delta H_{reaction}) = 0.001$ J; Series 1:$u(K) = 0.000002$ J/μV s, $u(\Delta_{mix}H) = 60.013$ J mol^{-1}; Series 2: $u(K) = 0.000002$ J/μV s, $u(\Delta_{mix}H) = 58.016$ Jmol^{-1}, Series 3: $u(K) = 0.000003$ J/μV s, $u(\Delta_{mix}H) = 62.008$ Jmol^{-1};

[b]T_D = drop temperature in Kelvin, T_M = bath temperature in Kelvin, n_{sn} = number of moles of tin, n_{Bi} = number of moles of bismuth, n_{sb} = number of moles of antimony, K = calibration constant, ΔH_{Signal} = the heat effect due to a single drop of sample to the bath, $\Delta_{mix}H$ = integral enthalpy of mixing of Sn-Bi-Sb system

$$\Delta H_{mix} = \sum_{i}\sum_{j>i}\left[x_i x_j \sum_{\upsilon} L_{i:j}^{(\upsilon)}\left(x_i - x_j\right)^{\upsilon}\right] + x_i x_j x_k\left(L_{i:j:k}^{0}x_{Sn} + L_{i:j:k}^{1}x_{Bi} + L_{i:j:k}^{2}x_{Sb}\right) \quad (4)$$

where $L_{i:j}^{(\upsilon)}(\nu = 0, 1, 2, \ldots)$ are the interaction parameters (binary) of the binary systems and $L_{i:j:k}^{\nu}$ $(\nu = 0, 1, 2, \ldots)$ are the interaction parameters (ternary). The mixing enthalpy obtained experimentally is compared with the calculated values considering the binary contributions only. The difference gives the ternary interaction contribution in this system, which is further optimized using Eq. 4. The ternary mixing enthalpy for Sn-Bi-Sb system for the cross-sections of $(Sb_{0.25}Bi_{0.75})_{1-x}Sn_x$, $(Sb_{0.50}Bi_{0.50})_{1-x}Sn_x$, $(Sb_{0.75}Bi_{0.25})_{1-x}Sn_x$, $(Sb_{0.50}Sn_{0.50})_{1-x}Bi_x$, $(Bi_{0.50}Sn_{0.50})_{1-x}Sb_x$

Table V Integral enthalpy of mixing values at the sites of intersection *a, b, c, d,* and *e*; see also Fig. 1

Intersection	Integral enthalpy of mixing in J/mol		
	Sn drops	Bi drops	Sb drops
a	− 80.032		− 87.534
b	212.632	208.551	
c	− 622.186		− 598.484
d	− 1104.138	− 1128.080	
e	− 488.278	− 472.155	− 476.945

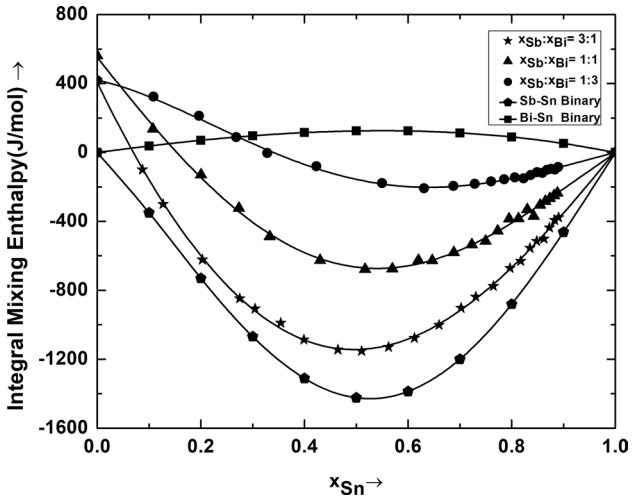

Fig. 2 The enthalpies of mixing of the given ternary alloy system corresponding to the cross-section of $(Sb_{0.25}Bi_{0.75})_{1-x}Sn_x$, circle; $(Sb_{0.50}Bi_{0.50})_{1-x}Sn_x$, triangle; and $(Sb_{0.75}Bi_{0.25})_{1-x}Sn_x$, star; at 973 K, Sb-Sn binary data from the literature,[38] pentagon; and Bi-Sn binary data from literature, square.[38]

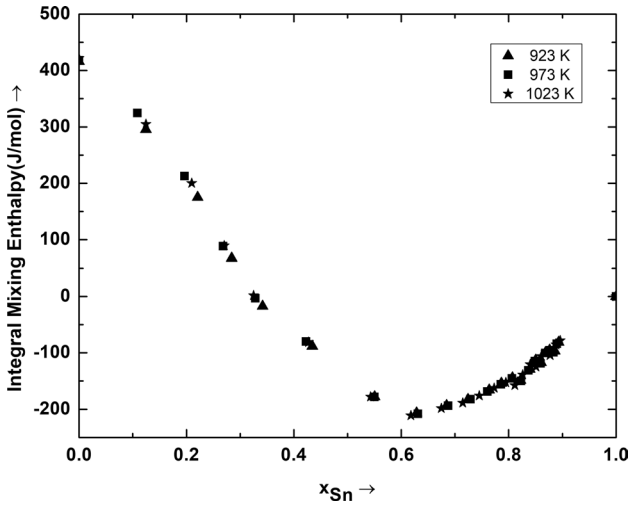

Fig. 3 The enthalpies of mixing of the given ternary alloy system for the cross-section of $(Sb_{0.25}Bi_{0.75})_{1-x}Sn_x$.

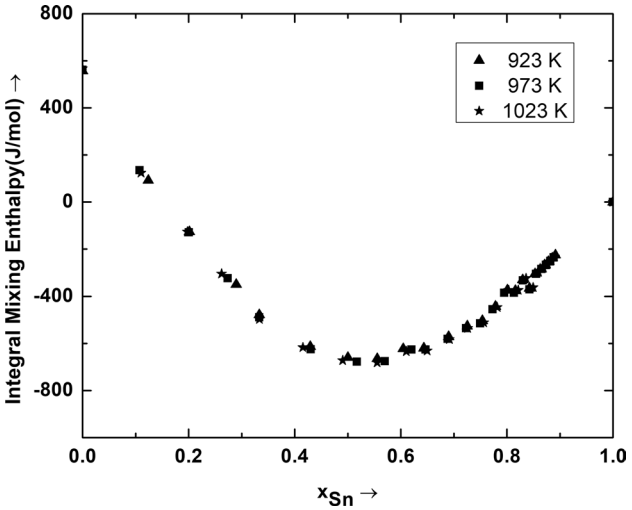

Fig. 4 The enthalpies of mixing of the given ternary alloy system for the cross-section of $(Sb_{0.50}Bi_{0.50})_{1-x}Sn_x$.

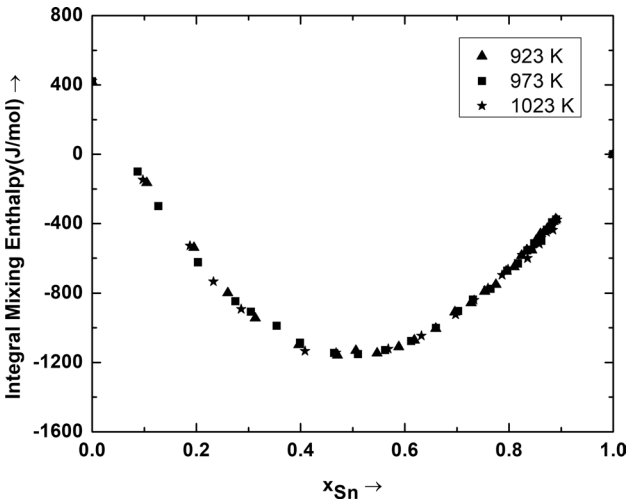

Fig. 5 The enthalpies of mixing of the given ternary alloy system for the cross-section of $(Sb_{0.75}Bi_{0.25})_{1-x}Sn_x$.

is represented in Fig. 11, along with the RKM modeled data fitted curve at 973 K as per Eq. 4.

The binary interaction parameters and findings from this study have been used to derive the ternary interaction parameters using the least square fit. The binary interaction parameters are taken from data in the literature[38] that was readily available. Table VI lists the interaction parameters for binary and ternary systems. The comparison between the experimental data with the values obtained from the RKM model considering the ternary interaction are shown in Fig. 11. It can be seen that both the values for the mixing enthalpies were in good agreement except for a few compositions. Therefore, the RKM substitutional model is very

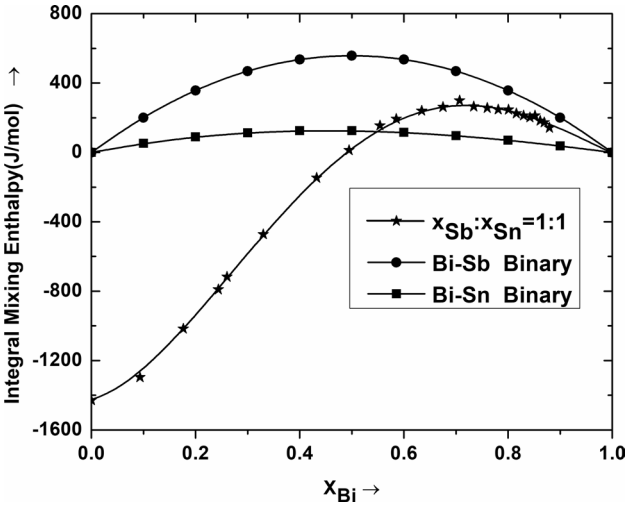

Fig. 6 The enthalpies of mixing of the given ternary alloy system for the cross-section of $(Sb_{0.50}Sn_{0.50})_{1-x}Bi_x$ at 973 K, star; Bi-Sb binary data from the literature,[38] circle; and Bi-Sn binary data from literature, square[38].

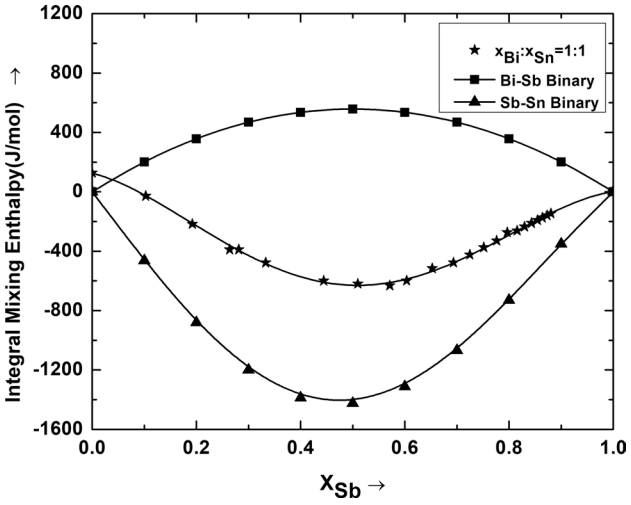

Fig. 8 The enthalpies of mixing of the given ternary alloy system for the cross-section of $(Bi_{0.50}Sn_{0.50})_{1-x}Sb_x$ at 973 K, star; Bi-Sb binary data from literature,[38] square; and Sb-Sn binary data from literature, triangle.[38]

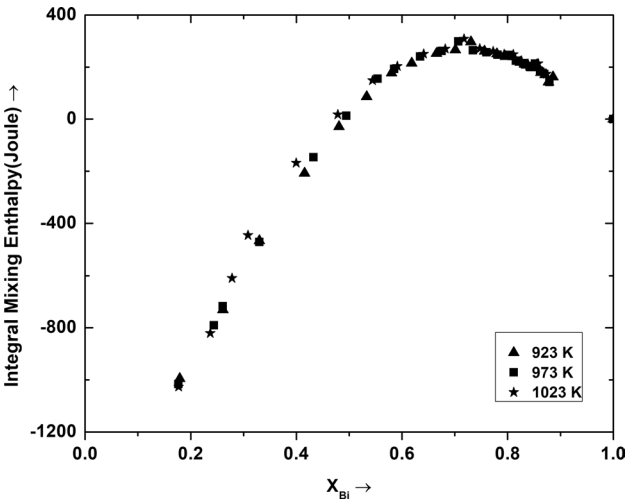

Fig. 7 The enthalpies of mixing of the given ternary alloy system for the cross-section of $(Sb_{0.50}Sn_{0.50})_{1-x}Bi_x$.

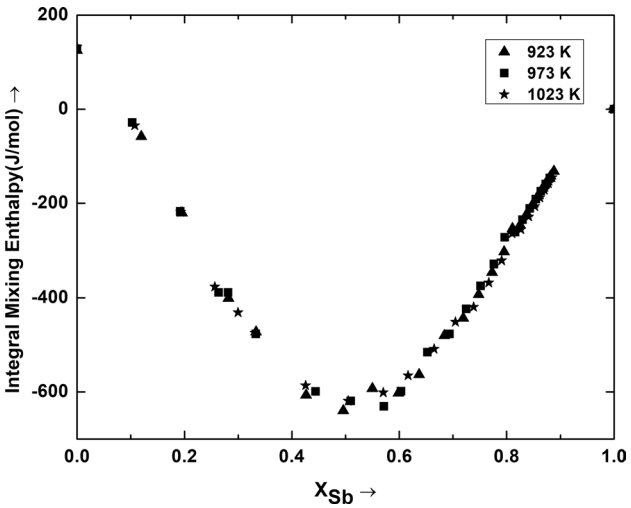

Fig. 9 The enthalpies of mixing of the given ternary alloy system for the cross-section of $(Bi_{0.50}Sn_{0.50})_{1-x}Sb_x$.

well followed by this system in the temperature range of 923–1023 K.

In Fig. 12, integral enthalpies of mixing for one of the five cross-sections $(Bi_{0.50}Sn_{0.50})_{1-x}Sb_x$ at 923 K, 973 K and 1023 K are plotted along with the literature data, [38]which were calculated using ternary interaction parameters of the boundary binaries of the ternary Bi-Sn-Sb system based on the RKM polynomial. It is inferred from Fig. 12 that the experimental results of the present investigations are in good agreement with the data reported in the literature.

Summary and Conclusions

Integral and partial mixing enthalpies of the Sn-Bi-Sb ternary system were investigated using a drop calorimeter in the temperature range of 923–1023 K along five of the cross-sections: $(Sb_{0.25}Bi_{0.75})_{1-x}Sn_x$, $(Sb_{0.50}Bi_{0.50})_{1-x}Sn_x$, $(Sb_{0.75}Bi_{0.25})_{1-x}Sn_x$, $(Sb_{0.50}Sn_{0.50})_{1-x}Bi_x$, $(Bi_{0.50}Sn_{0.50})_{1-x}Sb_x$ by drop methods. Pure Sb, Sn, and Bi were dropped into the crucible depending on the cross-sections. It has been found that the enthalpies of mixing are nearly temperature-independent.

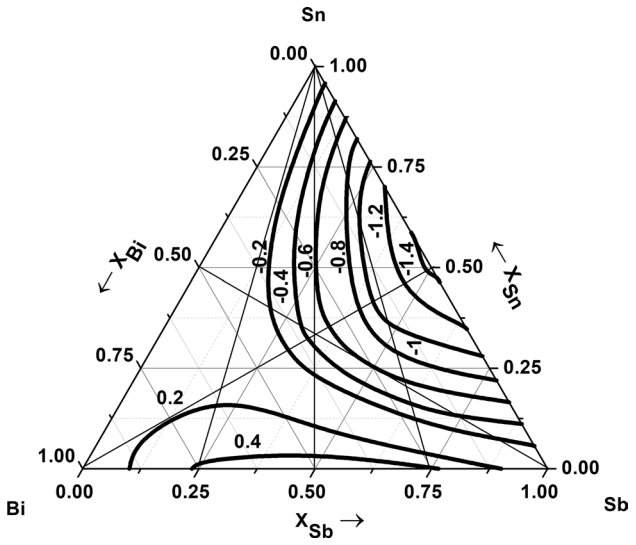

Fig. 10 Different iso-enthalpy curves of the given liquid ternary alloy at 973 K; values are in kJ/mol.

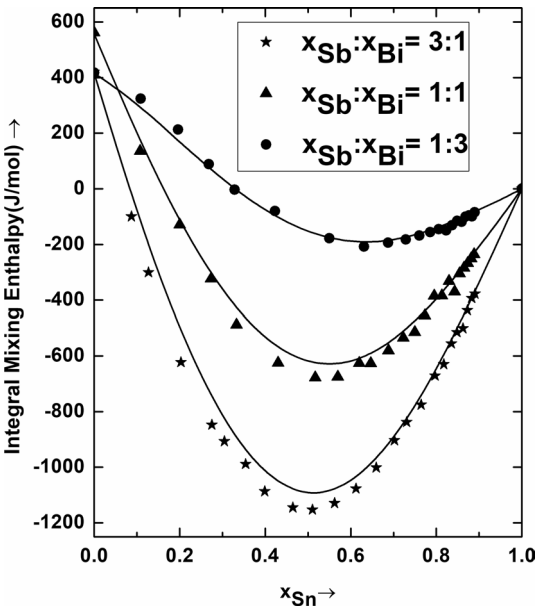

Fig. 11 Comparison of mixing enthalpies between RKM-modeled data, bold line, and experimental data of liquid Sn-Sb-Bi alloys along the cross-sections of $(Sb_{0.25}Bi_{0.75})_{1-x}Sn_x$, circle; $(Sb_{0.50}Bi_{0.50})_{1-x}Sn_x$, triangle; and $(Sb_{0.75}Bi_{0.25})_{1-x}Sn_x$, star; at 973 K.

The curves representing iso-enthalpy were plotted using the mixing enthalpy values for the all five cross-sections. Most of these curves were oriented towards the Sb-Sn binary system. This could be due to the stronger interatomic interaction between Sb and Sn atoms in the given sub-lattice of the given ternary system. Ternary interaction parameters were determined by using the RKM model, followed by least square optimization. The agreement between the experimental results and theoretical model was very good.

Table VI Binary and ternary interaction parameters

Interaction parameter	ν	J/mol
L^{ν}_{Bi-Sb} [38]	0	2230
L^{ν}_{Bi-Sn} [38]	0	500
	1	− 100
L^{ν}_{Sb-Sn} [38]	0	− 5695.1
	1	782.6
	2	1840.9
$L^{\nu}_{Sn-Bi-Sb}$	0	− 4743.1
	1	11251.87
	2	− 13969.1

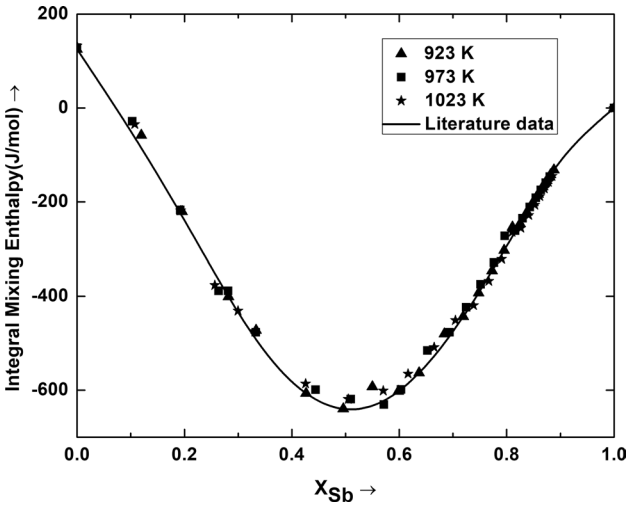

Fig. 12 Comparison of experimental results of this study with data available in the literature[38] along the cross-sections of $(Bi_{0.50}Sn_{0.50})_{1-x}Sb_x$ at 923 K, 973 K and 1023 K.

Conflict of interest The authors declare that they have no conflict of interest.

References

1. B.R. Allenby, Achieving sustainable development through industrial ecology, in *Proceeding of Surface Mount International Conference* (1992), pp. 1–28
2. D. Jaiswal, V. Singh, D. Pathote, and C.K. Behera, Electrochemical behaviour of lead-free Sn-0.7Cu-xIn solders alloys in 3.5 wt% NaCl solution. *J. Mater. Sci. Mater. Electron.* 32(18), 23371 (2021). https://doi.org/10.1007/s10854-021-06824-3.
3. M.R. Kumar, S. Mohan, and C.K. Behera, Measurements of mixing enthalpy for a lead-free solder Bi-In-Sn system. *J. Electron. Mater.* 48(12), 8096 (2019). https://doi.org/10.1007/s11664-019-07646-0.

4. M.R. Kumar, S. Mohan, and C.K. Behera, Thermodynamic accessment experimentally on Bi-Sn system by calorimeter. *Mater. Today Proc.* 5(14), 27777 (2018). https://doi.org/10.1016/j.matpr.2018.10.013.
5. D. Jaiswal, D. Pathote, V. Singh, and C.K. Behera, Electrochemical behaviour of lead-free Sn-In-Al solders alloys in 3.5 wt% NaCl solution. *Mater. Today Proc.* 57, 187 (2022). https://doi.org/10.1016/j.matpr.2022.02.315.
6. D. Pathote, D. Jaiswal, V. Singh, and C.K. Behera, Optimization of electrochemical corrosion behavior of 316L stainless steel as an effective biomaterial for orthopedic applications. *Mater. Today Proc.* 57, 265 (2022). https://doi.org/10.1016/j.matpr.2022.02.501.
7. M.R. Kumar, V. Singh, V.K. Rai, D. Jaiswal, and C.K. Behera, Investigation on mixing heat effect of bi-in and in-sn system at 730 K. *Mater. Today Proc.* 18, 2917 (2019). https://doi.org/10.1016/j.matpr.2019.07.161.
8. D. Jaiswal, D. Pathote, V. Singh, and C.K. Behera, Effect of Al addition on electrochemical behavior of Sn-0.7Cu-xAl lead-free solders alloys in 3.5 wt% NaCl solution. *J. Mater. Eng. Perform.* 31(9), 7550 (2022). https://doi.org/10.1007/s11665-022-06771-y.
9. J.S. Hwang, *Implementing Lead-Free Electronics* (New York: McGraw Hill Professional, 2004).
10. D. Pathote, D. Jaiswal, V. Singh, R.K. Gautam, and C.K. Behera, Wear behavior and microhardness studies of tantalum (Ta)-coated 316L stainless steel by DC magnetron sputtering for the orthopedic applications. *J. Mater. Sci.* (2022). https://doi.org/10.1007/s10853-022-07939-6.
11. S. Nagasaki and E. Fujita, Research on phase diagrams focusing on specific heat measurements (II) On solid solution energy and abnormal liquids. *J. Jpn. Inst. Met.* 16, 317 (1952).
12. W. Oelsen and K.F. Golucke, Thermodynamic study of In-Sn-Zn, Bi-Sn-Cu and Bi-Sn-Ni ternary systems as materials for lead-free soldering. *Arch. Eisenh Uttenwes* 289, 689 (1958).
13. H. Ohtani and K. Ishida, A thermodynamic study of the phase equilibria in the Bi-Sn-Sb system. *J. Electron. Mater.* 23, 747 (1994).
14. H.O. Samson, Heat content and heat of formation of molten alloys. *Z. Met.* 28, 197 (1936).
15. F.E. Wittig and F. Huber, Mixing enthalpies of Bi-Sn alloys. *Z. Electrochem.* 60, 1181 (1956).
16. A. Yazawa, T. Kawashima, and K. Itagaki, Measurements of heats of mixing in liquid alloys with the adiabatic calorimeter. *J. Jpn. Inst. Met.* 32, 1281 (1968).
17. R.L. Sharkey and M.J. Pool, Partial heats of mixing in the Bi-Sn system. *Met. Trans.* 3, 1773 (1972).
18. N. Asryan and A. Mikula, Thermodynamic properties of liquid Bi-Sn alloys. *Z. Met.* 95, 132 (2004).
19. A. Yazawa and K. Koike, Activity measurement in Sn-Pb, Sn-Bi, Sn-Tl and Sn-Pb-Bi alloys at 1100 C. *J. Min. Met. Inst. Jpn.* 184, 1593 (1968).
20. G. Rickert, P. Lamparterand, and S. Steeb, Activity measurement in Sn-Bi. *Zenaau Z. Natur. Tl. A* 31, 711 (1976).
21. H. Seltz and F.J. Dunkerley, A thermodynamic study of the Tin-Bismuth system. *J. Am. Chem. Soc.* 64, 1392 (1942).
22. B.J. Lee, C.S. Oh, and J.H. Shim, Thermodynamic assessments of the Sn-In and Sn-Bi binary systems. *J. Electron. Mater.* 25, 983 (1996).
23. M. Kawakami, The heat of mixing in molten metals. *Sci. Rep. Tohoku Imp. Univ.* 19, 521 (1930).
24. O.J. Kleppa, A calorimetric investigation of some binary and ternary liquid alloys rich in tin. *J. Phys. Chem.* 60, 842 (1956).
25. R. Hultgrcn, R.L. Orr, P.D. Anderson, and K.K. Kelley, *Selected Values of Thermodynamic Properties of Metals and Alloys* (New York: Wiley, 1963).
26. F. Sommer, R. Luck, N. Rupfbolz, and B. Predel, Chemical short-range order in liquid Sb-Sn alloys proved with the aid of the dependence of the mixing enthalpies on temperature. *Mater. Res. Bull.* 18, 621 (1983).
27. M. Azzaoui, M. Notin, and J. Hertz, Ternary experimental excess functions by means of high-order polynomials—enthalpy of mixing of liquid Pb-Sn-Sb alloys. *Z. Met.* 84, 545 (1993).
28. R.O. Frantik and H.J. Mcdonald, A thermodynamic study of the Tin-Antimony system. *Trans. Electrochem. Soc.* 88, 243 (1945).
29. V. Vassiliev, M. Lelaurain, and J. Hertz, A new proposal for the binary (Sn, Sb) phase diagram and its thermodynamic properties based on a new EMF study. *J. Alloy. Compd.* 247, 223 (1997).
30. S.W. Chen, C.C. Chen, W. Gierlotka, A.R. Zi, P.Y. Chen, and H.J. Wu, Phase equilibria of the Sn-Sb binary system. *J. Electron. Mater.* 37, 992 (2008).
31. M. Hansen and K. Anderko, *Constitution of Binary Alloys*, 2nd ed., (New York: McGraw-Hill Companies Inc, 1958).
32. S. Terlicka, A. Dębski, W. Gąsior, A. Fornalczyk, and M. Saternus, Experimental results of the Li-Pb-Pt system obtained by the high temperature drop calorimetry. *J. Mol. Liq.* 332, 115824 (2021). https://doi.org/10.1016/j.molliq.2021.115824.
33. D. Jendrzejczyk-Handzlik and P. Handzlik, Mixing enthalpies of liquid Au-Ga-In alloys. *J. Mol. Liq.* 301, 112439 (2020). https://doi.org/10.1016/j.molliq.2019.112439.
34. C.J. Smithells, *Metals Reference Book*, 3rd ed., (London: Butterworths, 1962).
35. O. Kubaschewski and W. Seith, Heat of formation of non-ferrous metal alloys. *Z. MetaUk.* 30, 7 (1938).
36. Y.E. Geguzin and B.Y. Pines, Heat of formation of Bi-Sb metal alloys. *Zhur. Fiz. Khim.* 26, 27 (1952).
37. I. Katayama, D. Zivkovic, D. Manasijevic, T. Tanaka, Z. Zivkovic, and H. Yamashita, Thermodynamic properties of liquid Sn-Bi-Sb alloys. *Netsu Sokutei* 32, 40 (2005).
38. D. Manasijevic, J. Vrestal, D. Minic, A. Kroupa, D. Zivkovic, and Z. Zivkovic, Phase equilibria and thermodynamics of the Bi-Sb-Sn ternary system. *J. Alloys Compd.* 438(1–2), 150 (2007). https://doi.org/10.1016/j.jallcom.2006.08.021.
39. O.E. Awe and O.M. Oshakuade, Theoretical prediction of thermodynamic activities of all components in the Bi-Sb-Sn ternary lead-free solder system and Pb-Bi-Sb-Sn quaternary system. *Thermochim. Acta* 589, 47 (2014). https://doi.org/10.1016/j.tca.2014.05.009.
40. C. Zhang, S.D. Liu, G.T. Qian, J. Zhou, and F. Xue, Effect of Sb content on properties of Sn-Bi solders. *Trans. Nonferrous Met. Soc. China (Engl. Ed.)* 24(1), 184 (2014). https://doi.org/10.1016/S1003-6326(14)63046-6.
41. A.V. Khvan, T. Babkina, A.T. Dinsdale, I.A. Uspenskaya, I.V. Fartushna, A.I. Druzhinina, A.B. Syzdykova, M.P. Belov, and I.A. Abrikosov, Thermodynamic properties of tin: part I experimental investigation, ab-initio modelling of α-, β-phase and a thermodynamic description for pure metal in solid and liquid state from 0 K. *Calphad Comput. Coupling Phase Diagr. Thermochem.* 65(December 2018), 50 (2019). https://doi.org/10.1016/j.calphad.2019.02.003.
42. I. Ansara and N. Dupin, *Cost 507 thermo chemical database for light metal alloys. European Commission DG X11* (Luxembourg: European Commission, 1998).

43. H. Ipser, H. Flandorfer, C.H. Luef, C. Schmetterer, and U. Saeed, Thermodynamics and phase diagrams of lead-free solder materials. *Lead-Free Electron. Solder. A Spec. Issue J. Mater. Sci. Mater. Electron.* (2007). https://doi.org/10.1007/978-0-387-48433-4_1.