



## Enthalpies of mixing of liquid Bi–Cu and Bi–Cu–Sn alloys relevant for lead-free soldering

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### ABSTRACT

Partial and integral enthalpies of mixing of liquid ternary Bi–Cu–Sn alloys at 800 °C were determined along nine sections in a large composition range. Additionally, binary alloys of the constituent binary system Bi–Cu were investigated at 800 and 1000 °C. Measurements were carried out using a Calvet-type microcalorimeter and a drop calorimetric technique. The binary data were evaluated by means of a standard Redlich–Kister polynomial fit whereas ternary data were fitted on the basis of an extended Redlich–Kister–Muggianu model for substitutional solutions.

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## 1. Introduction

The ROHS Directive of the European Union (“Directive on the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment 2002/95/EC”; see, for example Ref. [1]) became effective on 1 July 2006, with similar legislature active or impending in various other parts of the world. Due to this directive the use of lead is prohibited in electronic products, however, with a number of exemptions due to reliability issues [2]. One of them concerns the use of high-lead containing Pb–Sn solders (with Pb contents considerably higher than the eutectic composition) for so-called high-temperature soldering applications. This has initiated an extensive search for alternative alloy systems with melting temperatures higher than about 230 °C. As possible alternatives have been identified binary Ag–Bi or ternary Ag–Bi–Sn alloys. On the other hand, it has also been attempted to decrease the melting temperatures of Sn–Ag lead-free solders by adding small amounts of Bi [3]. Due to the frequent use of Cu as a substrate material in electronics, it is of importance to understand the interactions between these solders and the substrate, based on a sound knowledge of the phase equilibria in the system Bi–Cu–Sn and the quaternary Ag–Bi–Cu–Sn system.

One of the goals of the European COST Action 531 (“Lead-free Solder Materials”) has been the development of a thermodynamic database which contains the thermodynamic properties of various binary and ternary alloy systems, relevant for soldering, in a parametric form. Using commercially available standard software, the corresponding phase diagrams can be calculated based on the well-known CALPHAD method (see, for example, Ref. [28] and references therein). This database is currently being extended in the new COST Action MP 0602 (“Advanced Solder Materials for High Temperature Application”).

The present investigation is a contribution to this database. It wants to provide sound thermodynamic data for liquid Bi–Cu–Sn alloys which are urgently needed to optimize the thermodynamic parameters for this ternary system and to provide the basis for a reliable phase diagram calculation.

## 2. Bibliographic survey

The following section gives an overview over available literature data on the thermochemistry of ternary Bi–Cu–Sn alloys and the constituent binary systems, with special emphasis on the enthalpy of mixing of liquid alloys.

### 2.1. The Bi–Cu binary system

Several calorimetric investigations of the enthalpy of mixing of liquid Bi–Cu alloys can be found in the literature. In 1930, Kawakami

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[4] published the integral enthalpies of mixing at 1200 °C, although with a large scattering of the experimental values. Later, the binary system was investigated by Oelsen et al. [5] and Takeuchi et al. [6] at 1143 and 1342 °C, respectively. For Cu-rich alloys the results of the two latter investigations are in quite good agreement whereas significant lower enthalpy values were found by Takeuchi et al. [6] in the region towards Bi. On the other hand, Nikolskaya et al. [7] derived the enthalpy of mixing of liquid Bi–Cu alloys from their emf measurements. All these authors found a maximum in the enthalpy of mixing, however, with different absolute values and at different compositions: 6900 J/mol at 60 at.% Cu [4], 6100 J/mol at 50 at.% Cu [5], 5600 J/mol at 59 at.% Cu [6] and 6800 J/mol at 60 at.% Cu [7]. In general, there is no indication for any significant temperature dependence of the enthalpies of mixing.

There are two thermodynamic assessments of Bi–Cu in the literature, by Niemelä et al. [8] and Teppo et al. [9], both of the same research group. The enthalpies of mixing were calculated based on an optimized thermodynamic data set, and the calculated curves are nearly symmetrical with a maximum of about 6000 J/mol at 53 at.% Cu.

## 2.2. The Bi–Sn binary system

The enthalpy of mixing of liquid Bi–Sn alloys has been investigated several times by calorimetric methods, starting very early by Magnus and Mannheimer [10], later by Kawakami [11] and Samson-Himmelstjerna [12]. More recent results were reported by Wittig and Huber [13] at 470 °C, by Yazawa et al. [14] at 417 °C, and by Sharkey and Pool [15] at 452 °C. Azzaoui and Hertz [16] did calorimetric measurements at 508 °C between 0 and 42 at.% Bi. The corresponding values, derived from emf measurements, were reported by Seltz and Dunkerley [17] at 335 °C and, very recently, by Asryan and Mikula [18] at 450 °C.

Thermodynamic assessments of the Bi–Sn system were published by Lee et al. [19], using the well-known CALPHAD method, and by Cho and Ochoa [20] based on a so-called Chiotti integration.

Whereas the early experimental results [10–12] show large scattering, there is rather good agreement among the later investigations [13–15] with a maximum deviation of about 70 J/mol which is within the usual error limits of calorimetric techniques. Also the enthalpy values derived from emf measurements [17,18] and the assessed data by Lee et al. [19] are in satisfactory agreement with the experimental results mentioned before. Only the data given by Cho and Ochoa [20] deviate significantly, up to about 300 J/mol, from the other results. They are slightly exothermic, whereas all the other data published show an endothermic course of the integral enthalpy of mixing. For limiting binary values for our investigations in the ternary Bi–Cu–Sn system it was decided to choose the results by Asryan and Mikula [18], which are in good agreement with all the other experimental data and reveal the supposed non-regular behavior.

### 2.2.1. The Cu–Sn binary system

The enthalpy of mixing of liquid alloys in the Cu–Sn system has also been measured by calorimetry over the entire composition range and wide temperature ranges by several authors. Kawakami [4] was the first one to measure the enthalpy of mixing in liquid Cu–Sn alloys at 1200 °C, later followed Körber and Oelsen [21] at 1150 °C. Both applied direct reaction calorimetry. Using solution calorimetry, the enthalpies of mixing of liquid alloys were determined by Kleppa [22] at 450 °C, by Benz and Elliott [23] at 1127 °C, by Takeuchi et al. [6] at 1090 °C, by Itagaki and Yazawa [24] at 1100 °C, by Iguchi et al. [25] at 1120 °C and by Pool et al. [26] at 1167 °C. Recently, Lee et al. [27] reported experimental calorimetric values for 724 °C up to 60 at.% Cu.

Thermodynamic assessments have been published by Saunders and Miodownik [29], Shim et al. [30], and more recently, by Mietinen [31]. To describe the enthalpy of mixing of liquid alloys they included also values derived from emf-measurements at 1100 °C by Oishi et al. [32] and at 1300 °C by Ono et al. [33].

Basically, all the experimental values and calculated curves are in quite good agreement as far as the general shape of the curve is concerned, with  $\Delta_{\text{mix}}H$  values close to zero between 0 and 20 at.% Cu and a minimum at about 80 at.% Cu. However, the data given around this minimum differ significantly. The least exothermic values are those reported by Itagaki and Yazawa [24], with a minimum of about –3500 J/mol, and the most exothermic values were obtained by Iguchi et al. [25], with a minimum of about –6000 J/mol. These discrepancies cannot be explained by a possible temperature dependence of  $\Delta_{\text{mix}}H$  because the experimental temperatures of the two investigations are very similar. No systematic temperature dependence can be detected for the other experimental results.

In order to study a possible variation of  $\Delta_{\text{mix}}H$  with temperature, integral enthalpies of mixing of Cu–Sn alloys were determined at 500, 700, 900, 1100 and 1250 °C, respectively, by Flandorfer et al. [34]. Clearly more exothermic values were found at 500 °C, in excellent agreement with Kleppa [22] who measured at 450 °C up to 20 at.% Cu. Extrapolation of these data for metastable liquid alloys up to pure Cu resulted in a minimum of –8600 J/mol at 71 at.% Cu. However, no significant temperature dependence was observed at higher temperatures. The enthalpy of mixing over the entire composition range was determined at 1250 °C, with a minimum value of –4700 J/mol at 78 at.% Cu.

## 2.3. The Bi–Cu–Sn ternary system

To the best knowledge of the authors no data for the enthalpy of mixing of liquid alloys in the Bi–Cu–Sn ternary system are available from literature.

## 3. Experimental procedure

The calorimetric measurements were carried out in a Calvet-type twin microcalorimeter (SETARAM, Lyon, France; thermopile

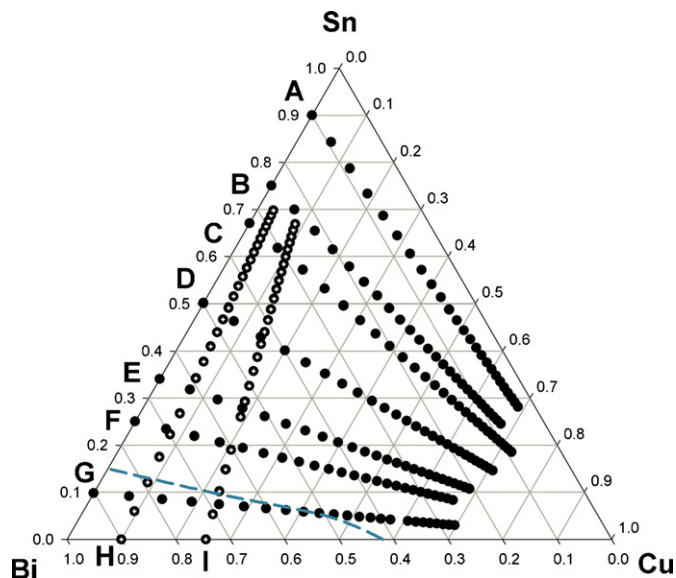


Fig. 1. Measured sections (A, B, . . . , I) and alloy compositions in the ternary Bi–Cu–Sn system at 800 °C; the liquidus limit is marked by the dashed grey line.

with more than 200 thermocouples, wire wound resistance furnace, automatic drop device for up to 30 drops, control and data evaluation with LabView HiQ as described by Flandorfer et al. [35]. To prevent oxidation, all measurements were performed under Ar flow (approximately 30 ml/min). The drop temperature (DT) and the temperature of the sample in the furnace ( $T_{\text{exp}}$ ) were measured before each drop. At the end of each series the calorimeter was calibrated by five drops (between 25 and 50 mg each) of standard  $\alpha\text{-Al}_2\text{O}_3$  (National Institute of Standards and Technology, Gaithersburg, MD).

The samples were prepared from Bi pellets (99.999%, ASARCO, South Plainfield, New Jersey, USA), Sn rods (99.998%, Alfa Johnson–Matthey, Karlsruhe, Germany), and Cu wire (99.98+ %, Goodfellow, Cambridge, UK). The Cu was treated under  $\text{H}_2$ -flow at 250 °C for 3 h to remove any oxide layers. Sn and Bi were used without further purification.

In a first step, the enthalpies of mixing of the Bi–Cu system were determined at 800 and 1000 °C. Small pieces (20–31 mg) of pure Cu were dropped into molten Bi (about 800 mg).

In the ternary Bi–Cu–Sn system, the enthalpies of mixing of about 240 molten samples were determined along nine different concentration sections at 800 °C, see Fig. 1. Pieces of pure Cu (18–35 mg) were dropped into about 700–800 mg of molten

$\text{Bi}_x\text{Sn}_{1-x}$  along seven sections ( $x=0.10; 0.25; 0.33; 0.50; 0.66; 0.75; 0.90$ ). To cross-check the enthalpies of mixing at several intersections, pure Sn was also dropped into molten  $\text{Bi}_x\text{Cu}_{1-x}$  alloys along two sections with  $x=0.75$  and 0.90, respectively. Attempts to drop Bi in molten Cu–Sn alloys were not successful because parts of the Bi pieces stuck at the end of the inner glass tube above the crucible without mixing with the liquid alloy in it. Obviously, the Bi pieces start to melt immediately by touching the inner glass tube.

The interval between individual drops was usually 40 min, and the heat flow acquisition interval was about 0.73 s. The obtained signals were recorded and integrated. The measured enthalpy (integrated heat flow at constant pressure) is as follows:

$$\Delta H_{\text{signal}} = n_i [H_{i(l), T_{\text{exp}}} - H_{i(s), \text{DT}}] + \Delta H_{\text{reaction}} \quad (1)$$

where  $n_i$  is the number of moles of the dropped element  $i$ ,  $H_{i(l), T_{\text{exp}}}$  is the molar enthalpy of the liquid element  $i$  at the experimental temperature  $T_{\text{exp}}$  (Kelvin) and  $H_{i(s), \text{DT}}$  the molar enthalpy of the solid element  $i$  at the drop temperature. The difference  $H_{i(l), T_{\text{exp}}} - H_{i(s), \text{DT}}$  was calculated using the Dinsdale polynomials for the thermodynamic data of pure elements [36]. For the respective temperatures (DT and  $T_{\text{exp}}$ ) the average of the values for each individual drop of a series of experiments was taken because their scatter was low enough. Because of the rather small masses added, the partial

**Table 1**

Partial and integral enthalpies of liquid Bi–Cu alloys at 800 °C

Mole dropped, $n_{\text{Cu}}$ (mmol)	Heat effect, $\Delta H_{\text{signal}}$ (J/mol)	Partial enthalpy		Integral enthalpy	
		$x_{\text{Cu}}^a$	$\Delta_{\text{mix}} \bar{H}$ (J/mol)	$x_{\text{Cu}}$	$\Delta_{\text{mix}} H$ (J/mol)
1st run, starting amount: $n(\text{Bi}) = 3.8798$ mmol					
0.3142	16,465	0.0375	18,801	0.0749	1,409
0.3262	16,103	0.1083	15,771	0.1417	2,445
0.3604	16,646	0.1734	12,590	0.2051	3,194
0.3967	17,330	0.2349	10,092	0.2648	3,713
0.3987	16,913	0.2906	8,826	0.3165	4,072
0.4075	16,508	0.3393	6,912	0.3622	4,262
0.4175	16,327	0.3827	5,510	0.4032	4,342
0.4259	12,561	0.4216	−4,106	0.4399	3,823
0.4342	8,785	0.4564	−13,363	0.4729	2,809
0.4480	8,928	0.4881	−13,668	0.5032	1,864
0.4485	8,956	0.5167	−13,626	0.5302	1,023
0.4532	9,168	0.5424	−13,367	0.5546	274
0.4568	9,338	0.5657	−13,150	0.5768	−395
0.4639	9,328	0.5870	−13,488	0.5972	−1,026
0.4718	9,504	0.6066	−13,450	0.6160	−1,606
0.4870	9,984	0.6248	−13,093	0.6336	−2,134
0.4934	9,738	0.6418	−13,857	0.6500	−2,656
2nd run, starting amount: $n(\text{Bi}) = 6.2860$ mmol					
0.2802	14,613	0.0213	19,041	0.0427	813
0.2804	14,162	0.0623	17,496	0.0819	1,496
0.2838	13,823	0.1002	15,691	0.1184	2,061
0.2862	13,454	0.1354	14,016	0.1524	2,522
0.2986	13,596	0.1688	12,725	0.1852	2,917
0.3030	13,247	0.2006	11,120	0.2160	3,227
0.3031	13,066	0.2303	10,481	0.2446	3,491
0.3163	13,400	0.2584	10,024	0.2722	3,730
0.3190	13,223	0.2852	9,040	0.2982	3,920
0.3261	13,323	0.3105	8,380	0.3228	4,076
0.3305	13,156	0.3345	7,346	0.3461	4,189
0.3383	13,347	0.3572	6,989	0.3683	4,284
0.3408	13,192	0.3788	6,318	0.3893	4,351
0.3479	11,109	0.3992	−521	0.4092	4,192
0.3498	9,195	0.4186	−6,263	0.4280	3,859
0.3530	7,555	0.4369	−11,123	0.4458	3,393
0.3579	7,139	0.4543	−12,599	0.4628	2,904
0.3600	6,971	0.4708	−13,203	0.4788	2,423
0.3638	7,022	0.4864	−13,207	0.4941	1,965

Standard states: pure liquid components.

<sup>a</sup> Under the assumption of a nearly linear course of the partial enthalpy between two drops the respective enthalpy values have been allocated to the mean value of the concentrations before and after the drop.

**Table 2**  
Partial and integral enthalpies of liquid Bi–Cu alloys at 1000 °C

Mole dropped, $n_{Cu}$ (mmol)	Heat effect, $\Delta H_{signal}$ (J/mol)	Partial enthalpy		Integral enthalpy	
		$x_{Cu}$	$\Delta_{mix}\bar{H}$ (J/mol)	$x_{Cu}$	$\Delta_{mix}H$ (J/mol)
Starting amount: $n(Bi) = 3.27205$ mmol					
0.4437	25,234	0.0597	17,372	0.1194	2,074
0.4704	25,585	0.1689	14,892	0.2184	3,515
0.4774	24,411	0.2584	11,630	0.2984	4,345
0.4878	23,712	0.3316	9,107	0.3648	4,796
0.4886	23,090	0.3923	7,753	0.4198	5,052
0.5339	24,396	0.4449	6,189	0.4700	5,151
0.5344	24,020	0.4911	5,445	0.5122	5,174
0.5404	23,769	0.5304	4,483	0.5486	5,123
0.5436	23,582	0.5643	3,880	0.5801	5,036
0.5496	23,752	0.5939	3,717	0.6078	4,949
0.5502	23,498	0.6199	3,203	0.6320	4,841
0.5515	23,303	0.6428	2,753	0.6535	4,719
0.5612	23,570	0.6632	2,496	0.6730	4,594
0.5656	23,553	0.6817	2,143	0.6904	4,463
0.6250	26,062	0.6991	2,195	0.7077	4,337
0.6606	27,529	0.7159	2,171	0.7240	4,216
0.6942	29,140	0.7316	2,477	0.7393	4,120
0.7100	29,376	0.7463	1,870	0.7532	3,999
0.7143	29,198	0.7595	1,377	0.7659	3,865
0.7172	29,467	0.7716	1,583	0.7773	3,754
0.7712	31,824	0.7828	1,763	0.7884	3,655
0.7739	32,440	0.7934	2,418	0.7985	3,596
0.7876	31,694	0.8031	740	0.8078	3,463
0.8009	32,463	0.8121	1,032	0.8164	3,354
0.8044	32,515	0.8204	920	0.8244	3,249

Standard states: pure liquid components.

enthalpies can be calculated directly as follows:

$$h_i \approx \frac{\Delta H_{reaction}}{n_i} \quad (2)$$

Random errors as well as systematic errors of calorimetry depend on the construction of the calorimeter, calibration procedure, signal integration and “chemical errors”, e.g. incomplete reactions or impurities. Considering many calibration measurements dropping NIST standard sapphire we can estimate the standard deviation to be less than  $\pm 1\%$ . The systematic errors are mainly caused by parasitic heat flows, base line problems at signal integration and dropping and mixing problems. Most of these error contributions are in terms of absolute values and usually weight out the random errors. It can be estimated to be  $\pm 150$  J/mol for measurements at  $T \leq 1000$  °C.

## 4. Results and discussion

### 4.1. Experimental results

The experimental data for the investigated sections in the systems Bi–Cu and Bi–Cu–Sn are collected in Tables 1–4. These tables contain all the necessary experimental information like starting amounts, added amounts, and the corresponding heat effects as well as the calculated partial and integral enthalpies of mixing of the liquid alloys.

Fig. 2 shows the experimental data of the integral molar enthalpy of mixing for the Bi–Cu system at 800 and 1000 °C. The higher temperature of 1000 °C was chosen to be able to cover a larger liquid composition range and, in addition, to check for a possible temperature dependence. All measured enthalpies of mixing are endothermic. The experimental values were fitted using the well-known Redlich–Kister polynomials with two interaction parameters  ${}^{(0)}L$  and  ${}^{(1)}L$  (see Table 5). The fitted curves show both

a maximum at 50 at.% Bi and 4000 J/mol (800 °C) and 5000 J/mol (1000 °C). This implies a slight but significant temperature dependence of  $\Delta_{mix}H$  in the Bi–Cu system. At 800 °C, the kink in the composition dependence of the experimental data at about 60 at.% Bi indicates the precipitation of the (Cu) phase. This is in good agreement with the liquidus point at this temperature in the current version of the phase diagram [37].

Figs. 3 and 4 show as an example the integral and the partial enthalpy of mixing along section G (pure Cu dropped into liquid  $Bi_{0.9}Sn_{0.1}$ ). The enthalpy of mixing shows a kink at approximately 55 at.% Cu which is in accordance with a sudden drop of the partial values at about the same concentration. This is caused by the pri-

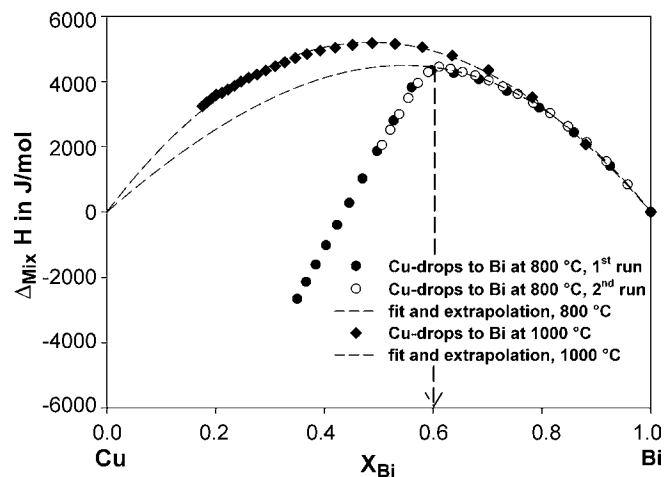


Fig. 2. Integral molar enthalpies in liquid Bi–Cu alloys at 800 and 1000 °C, standard states: pure liquid metals.

**Table 3**  
 Partial and integral enthalpies of liquid Bi–Cu–Sn alloys at 800 °C

Mole dropped, $n_{\text{Cu}}$ (mmol)	Heat effect $\Delta H_{\text{signal}}$ (J/mol)	Partial enthalpy		Integral enthalpy		
		$x_{\text{Cu}}$	$\Delta_{\text{mix}}\bar{H}$ (J/mol)	$x_{\text{Bi}}$	$x_{\text{Cu}}$	$\Delta_{\text{mix}}H$ (J/mol)
Section A, starting amounts: $n(\text{Bi}) = 0.5338$ mmol; $n(\text{Sn}) = 4.8046$ mmol						
0.3621	12,901	0.0318	1,968	0.0936	0.0635	160
0.4044	13,858	0.0945	610	0.0874	0.1256	190
0.4465	14,688	0.1553	–758	0.0815	0.1851	125
0.4479	14,249	0.2112	–1,844	0.0763	0.2373	–1
0.4582	14,152	0.2607	–2,776	0.0716	0.2842	–171
0.4742	14,141	0.3056	–3,835	0.0673	0.3269	–390
0.4748	13,837	0.3460	–4,517	0.0635	0.3650	–623
0.4763	13,541	0.3820	–5,227	0.0601	0.3990	–870
0.4783	13,342	0.4144	–5,766	0.0570	0.4297	–1,120
0.4825	13,174	0.4437	–6,353	0.0542	0.4577	–1,377
0.4849	12,818	0.4704	–7,225	0.0517	0.4831	–1,651
0.4906	12,781	0.4949	–7,603	0.0493	0.5066	–1,921
0.4912	12,590	0.5173	–8,029	0.0472	0.5280	–2,186
0.4919	12,484	0.5378	–8,278	0.0452	0.5477	–2,440
0.4930	12,364	0.5567	–8,580	0.0434	0.5658	–2,687
0.5013	12,409	0.5743	–8,907	0.0417	0.5828	–2,930
0.5033	12,518	0.5907	–8,786	0.0401	0.5986	–3,152
0.5171	12,749	0.6061	–9,005	0.0386	0.6136	–3,371
0.5213	13,051	0.6207	–8,626	0.0372	0.6277	–3,562
0.5358	13,126	0.6344	–9,159	0.0359	0.6411	–3,764
0.5427	13,318	0.6474	–9,116	0.0346	0.6537	–3,952
0.5457	13,265	0.6596	–9,352	0.0334	0.6656	–4,137
0.5479	13,430	0.6711	–9,146	0.0323	0.6767	–4,303
0.5499	13,340	0.6819	–9,399	0.0313	0.6871	–4,467
Section B, 1st run, starting amounts: $n(\text{Bi}) = 1.4125$ mmol; $n(\text{Sn}) = 4.2460$ mmol						
0.4120	15,661	0.0339	4,229	0.2327	0.0679	360
0.4158	15,090	0.0977	2,506	0.2178	0.1276	498
0.4216	14,796	0.1542	1,309	0.2045	0.1809	547
0.4336	14,660	0.2051	21	0.1924	0.2292	516
0.4359	14,439	0.2508	–663	0.1816	0.2724	450
0.4387	13,904	0.2919	–2,096	0.1719	0.3113	314
0.4422	13,758	0.3289	–2,673	0.1631	0.3465	162
0.4476	13,488	0.3625	–3,652	0.1551	0.3786	–26
0.4520	13,414	0.3933	–4,110	0.1478	0.4080	–219
0.4627	13,569	0.4216	–4,460	0.1410	0.4353	–415
0.4674	13,371	0.4479	–5,178	0.1347	0.4605	–627
0.4712	13,341	0.4721	–5,475	0.1289	0.4837	–836
0.4784	13,226	0.4945	–6,141	0.1235	0.5053	–1,058
0.4785	13,187	0.5152	–6,228	0.1185	0.5251	–1,265
0.4791	12,914	0.5343	–6,833	0.1140	0.5435	–1,480
0.4792	12,780	0.5520	–7,114	0.1097	0.5605	–1,690
0.4798	12,724	0.5684	–7,269	0.1058	0.5763	–1,890
0.4806	12,602	0.5836	–7,564	0.1021	0.5910	–2,088
0.4824	12,624	0.5979	–7,618	0.0987	0.6048	–2,274
0.4833	12,665	0.6112	–7,583	0.0954	0.6177	–2,447
0.4883	12,896	0.6238	–7,378	0.0924	0.6299	–2,605
0.4962	12,925	0.6357	–7,739	0.0895	0.6415	–2,766
0.5037	12,235	0.6471	–9,495	0.0867	0.6526	–2,974
0.5151	12,447	0.6579	–9,622	0.0841	0.6633	–3,178
0.5354	12,955	0.6685	–9,587	0.0815	0.6737	–3,376
Section B, 2nd run, starting amounts: $n(\text{Bi}) = 0.2497$ mmol; $n(\text{Sn}) = 0.7503$ mmol						
0.3755	14,589	0.0312	5,170	0.2342	0.0623	396
0.3789	14,116	0.0900	3,575	0.2203	0.1178	584
0.3797	13,578	0.1425	2,082	0.2080	0.1671	667
0.3837	13,415	0.1894	1,281	0.1969	0.2117	700
0.3995	13,428	0.2325	–63	0.1865	0.2533	660
0.4082	13,428	0.2724	–781	0.1769	0.2915	586
0.4209	13,478	0.3093	–1,654	0.1681	0.3270	474
0.4306	13,466	0.3434	–2,406	0.1599	0.3599	334
0.4337	13,167	0.3748	–3,317	0.1524	0.3898	163
0.4462	13,247	0.4038	–3,990	0.1454	0.4179	–28
0.4510	13,280	0.4308	–4,233	0.1389	0.4437	–215
0.4607	13,244	0.4558	–4,927	0.1329	0.4678	–419
0.4659	13,212	0.4790	–5,322	0.1273	0.4902	–625
0.4750	13,295	0.5007	–5,688	0.1221	0.5112	–833
0.4824	13,415	0.5209	–5,865	0.1172	0.5307	–1,035
0.4927	13,526	0.5400	–6,223	0.1126	0.5492	–1,239
0.4979	13,387	0.5578	–6,791	0.1083	0.5664	–1,451
0.4987	13,375	0.5744	–6,856	0.1043	0.5824	–1,650
0.5116	13,615	0.5900	–7,063	0.1005	0.5976	–1,847
0.5257	13,946	0.6048	–7,151	0.0969	0.6121	–2,039
0.5260	13,784	0.6189	–7,474	0.0935	0.6256	–2,228

Table 3 (Continued)

Mole dropped, $n_{\text{Cu}}$ (mmol)	Heat effect $\Delta H_{\text{signal}}$ (J/mol)	Partial enthalpy		Integral enthalpy		
		$x_{\text{Cu}}$	$\Delta_{\text{mix}}\bar{H}$ (J/mol)	$x_{\text{Bi}}$	$x_{\text{Cu}}$	$\Delta_{\text{mix}}H$ (J/mol)
0.5264	13,832	0.6319	-7,398	0.0903	0.6382	-2,402
0.5270	13,269	0.6441	-8,497	0.0874	0.6500	-2,601
0.5286	12,761	0.6556	-9,537	0.0846	0.6611	-2,821
0.5383	12,996	0.6664	-9,533	0.0820	0.6717	-3,031
Section C, starting amounts: $n(\text{Bi}) = 1.5342$ mmol; $n(\text{Sn}) = 3.1188$ mmol						
0.3925	15,682	0.0389	6,161	0.3041	0.0778	565
0.4105	15,572	0.1125	4,138	0.2812	0.1472	833
0.4122	14,906	0.1771	2,370	0.2614	0.2071	941
0.4156	14,464	0.2333	1,013	0.2442	0.2595	946
0.4172	13,855	0.2826	-584	0.2290	0.3056	851
0.4374	14,049	0.3269	-1,673	0.2149	0.3482	696
0.4557	14,182	0.3677	-2,673	0.2020	0.3873	494
0.4741	14,297	0.4053	-3,641	0.1902	0.4233	251
0.4872	14,365	0.4397	-4,308	0.1793	0.4561	-9
0.4902	14,133	0.4709	-4,966	0.1696	0.4856	-277
0.4913	13,833	0.4988	-5,639	0.1609	0.5121	-554
0.5008	13,933	0.5243	-5,977	0.1528	0.5364	-824
0.5019	13,537	0.5475	-6,825	0.1456	0.5585	-1,110
0.5042	12,739	0.5686	-8,529	0.1389	0.5787	-1,449
0.5077	12,318	0.5879	-9,532	0.1328	0.5972	-1,804
0.5082	11,861	0.6057	-10,455	0.1272	0.6142	-2,168
0.5083	12,312	0.6220	-9,574	0.1221	0.6298	-2,468
0.5085	12,044	0.6370	-10,109	0.1173	0.6442	-2,765
0.5151	12,588	0.6509	-9,360	0.1129	0.6577	-3,015
0.5198	12,983	0.6640	-8,817	0.1087	0.6703	-3,229
0.5309	13,659	0.6762	-8,070	0.1048	0.6822	-3,404
0.5355	14,124	0.6878	-7,422	0.1011	0.6934	-3,546
0.5359	14,407	0.6987	-6,913	0.0976	0.7039	-3,661
0.5427	15,205	0.7088	-5,780	0.0944	0.7138	-3,732
0.5454	15,496	0.7184	-5,381	0.0913	0.7231	-3,785
Section D, 1st run, starting amounts: $n(\text{Bi}) = 2.4003$ mmol; $n(\text{Sn}) = 2.4116$ mmol						
0.3887	16,679	0.0374	9,205	0.4615	0.0747	785
0.4017	16,344	0.1079	6,981	0.4285	0.1411	1229
0.4087	15,729	0.1703	4,774	0.3993	0.1995	1470
0.4119	15,087	0.2251	2,914	0.3737	0.2508	1563
0.4316	14,972	0.2744	976	0.3502	0.2980	1526
0.4352	14,552	0.3190	-273	0.3293	0.3399	1418
0.4504	14,430	0.3591	-1,668	0.3101	0.3783	1239
0.4532	14,179	0.3955	-2,425	0.2930	0.4127	1036
0.4599	13,501	0.4283	-4,357	0.2774	0.4439	749
0.4622	12,958	0.4580	-5,676	0.2633	0.4721	424
0.4632	11,224	0.4849	-9,480	0.2506	0.4976	-55
0.4653	10,783	0.5093	-10,534	0.2390	0.5209	-541
0.4717	11,291	0.5317	-9,772	0.2283	0.5424	-955
0.4718	11,255	0.5522	-9,852	0.2185	0.5621	-1,337
0.4756	11,858	0.5711	-8,778	0.2094	0.5802	-1,646
0.4841	12,183	0.5887	-8,545	0.2009	0.5972	-1,925
0.4966	13,156	0.6053	-7,217	0.1929	0.6133	-2,136
0.4974	13,295	0.6207	-6,983	0.1855	0.6282	-2,323
0.4976	13,654	0.6351	-6,269	0.1786	0.6419	-2,469
0.4985	14,223	0.6483	-5,177	0.1722	0.6547	-2,566
0.4989	14,702	0.6607	-4,242	0.1663	0.6667	-2,624
0.5002	14,996	0.6723	-3,729	0.1607	0.6778	-2,661
0.5089	15,507	0.6831	-3,236	0.1554	0.6885	-2,680
0.5151	16,141	0.6935	-2,374	0.1504	0.6985	-2,670
0.5420	17,136	0.7035	-2,094	0.1455	0.7084	-2,651
Section D, 2nd run, starting amounts: $n(\text{Bi}) = 2.3982$ mmol; $n(\text{Sn}) = 2.3969$ mmol						
0.4029	17,255	0.0388	9,227	0.4614	0.0775	812
0.4091	16,648	0.1112	7,095	0.4277	0.1448	1,270
0.4229	16,222	0.1748	4,758	0.3977	0.2048	1,515
0.4253	15,575	0.2310	3,021	0.3715	0.2572	1,614
0.4291	15,041	0.2803	1,453	0.3483	0.3035	1,604
0.4327	14,458	0.3241	-185	0.3277	0.3447	1,498
0.4400	14,092	0.3633	-1,569	0.3092	0.3819	1,324
0.4454	13,878	0.3986	-2,442	0.2924	0.4154	1,120
0.4551	13,395	0.4308	-4,167	0.2770	0.4462	842
0.4650	12,797	0.4603	-6,078	0.2629	0.4744	489
0.4682	11,026	0.4872	-10,050	0.2500	0.5000	-25
0.4707	10,676	0.5117	-10,916	0.2383	0.5234	-535
0.4735	11,443	0.5341	-9,430	0.2276	0.5449	-935
0.4763	11,509	0.5547	-9,432	0.2178	0.5645	-1,302
0.4767	12,109	0.5736	-8,196	0.2088	0.5826	-1,588
0.4768	12,252	0.5909	-7,903	0.2004	0.5992	-1,840
0.4838	12,630	0.6070	-7,493	0.1926	0.6148	-2,060

Table 3 (Continued)

Mole dropped, $n_{\text{Cu}}$ (mmol)	Heat effect $\Delta H_{\text{signal}}$ (J/mol)	Partial enthalpy		Integral enthalpy		
		$x_{\text{Cu}}$	$\Delta_{\text{mix}}\bar{H}$ (J/mol)	$x_{\text{Bi}}$	$x_{\text{Cu}}$	$\Delta_{\text{mix}}H$ (J/mol)
0.4844	13,240	0.6220	-6,267	0.1854	0.6292	-2,217
0.4894	13,546	0.6360	-5,921	0.1787	0.6428	-2,352
0.4917	13,892	0.6491	-5,346	0.1724	0.6554	-2,458
0.4955	14,583	0.6613	-4,169	0.1664	0.6672	-2,517
1.0106	30,536	0.6781	-3,384	0.1555	0.6890	-2,574
0.5124	16,011	0.6940	-2,348	0.1505	0.6990	-2,566
0.5143	16,139	0.7038	-2,218	0.1458	0.7085	-2,556
Section E, starting amounts: $n(\text{Bi}) = 2.8753$ mmol; $n(\text{Sn}) = 1.4862$ mmol						
0.3115	14,402	0.0333	12,630	0.6153	0.0667	930
0.3299	14,354	0.0974	9,916	0.5747	0.1282	1,522
0.3368	13,906	0.1557	7,689	0.5385	0.1832	1,911
0.3428	13,441	0.2078	5,614	0.5060	0.2325	2,135
0.3702	13,772	0.2559	3,606	0.4751	0.2794	2,225
0.3825	13,610	0.3008	1,984	0.4468	0.3222	2,210
0.3852	12,246	0.3414	-1,805	0.4216	0.3605	1,983
0.3871	9,757	0.3777	-8,392	0.3989	0.3949	1,426
0.3925	9,412	0.4105	-9,619	0.3783	0.4261	856
0.3926	9,713	0.4402	-8,858	0.3598	0.4543	379
0.3926	10,052	0.4671	-7,995	0.3429	0.4798	-13
0.3934	10,382	0.4915	-7,207	0.3275	0.5032	-336
0.3967	10,932	0.5139	-6,042	0.3134	0.5246	-582
0.3970	11,344	0.5345	-5,023	0.3004	0.5444	-767
0.3979	11,698	0.5534	-4,200	0.2884	0.5625	-904
0.4087	12,389	0.5712	-3,289	0.2770	0.5798	-998
0.4148	12,789	0.5878	-2,767	0.2664	0.5959	-1,066
0.4180	13,245	0.6034	-1,915	0.2565	0.6110	-1,097
0.4308	13,846	0.6182	-1,460	0.2470	0.6254	-1,111
0.4320	14,302	0.6321	-495	0.2381	0.6388	-1,089
0.4383	14,936	0.6451	477	0.2298	0.6514	-1,034
0.4406	15,112	0.6574	696	0.2220	0.6633	-975
0.4447	15,585	0.6689	1,448	0.2146	0.6745	-895
0.4460	15,910	0.6797	2,073	0.2077	0.6850	-799
Section F, starting amounts: $n(\text{Bi}) = 3.1343$ mmol; $n(\text{Sn}) = 1.0487$ mmol						
0.2917	14,189	0.0326	15,121	0.7004	0.0652	1,059
0.3025	13,916	0.0948	12,480	0.6561	0.1244	1,782
0.3083	13,537	0.1509	10,388	0.6163	0.1775	2,304
0.3169	13,049	0.2016	7,657	0.5802	0.2257	2,618
0.3246	12,794	0.2476	5,896	0.5473	0.2696	2,804
0.3251	11,949	0.2892	3,230	0.5179	0.3088	2,827
0.3257	10,171	0.3265	-2,300	0.4914	0.3441	2,565
0.3290	8,637	0.3602	-7,271	0.4673	0.3763	2,082
0.3368	9,107	0.3912	-6,482	0.4450	0.4061	1,673
0.3373	9,131	0.4197	-6,452	0.4247	0.4333	1,301
0.3691	10,528	0.4468	-5,001	0.4044	0.4602	1,001
0.3701	10,946	0.4725	-3,946	0.3860	0.4848	776
0.3741	11,436	0.4962	-2,957	0.3690	0.5075	611
0.3763	11,741	0.5180	-2,322	0.3533	0.5284	487
0.3871	12,532	0.5383	-1,152	0.3386	0.5481	419
0.3895	12,957	0.5573	-259	0.3249	0.5664	391
0.3960	13,149	0.5749	-324	0.3121	0.5835	363
0.3970	13,851	0.5914	1,363	0.3002	0.5993	401
0.4124	14,549	0.6069	1,755	0.2888	0.6146	452
0.4207	15,087	0.6217	2,335	0.2780	0.6289	523
0.4257	15,310	0.6357	2,442	0.2679	0.6424	593
0.4264	15,779	0.6487	3,485	0.2585	0.6550	694
0.4272	14,801	0.6609	1,122	0.2497	0.6668	709
Section G, 1st run, starting amounts: $n(\text{Bi}) = 3.3836$ mmol; $n(\text{Sn}) = 0.3684$ mmol						
0.2755	13,850	0.0342	16,752	0.8401	0.0684	1,180
0.2974	14,132	0.1004	13,984	0.7824	0.1325	2,061
0.3026	13,466	0.1608	10,969	0.7312	0.1892	2,643
0.3245	13,870	0.2158	9,210	0.6833	0.2423	3,074
0.3326	13,419	0.2662	6,814	0.6403	0.2900	3,309
0.3395	13,082	0.3114	4,999	0.6016	0.3329	3,411
0.3412	12,750	0.3520	3,840	0.5672	0.3710	3,436
0.3415	12,374	0.3881	2,704	0.5365	0.4051	3,396
0.3418	12,167	0.4204	2,069	0.5089	0.4357	3,328
0.3463	12,200	0.4496	1,701	0.4837	0.4636	3,247
0.3526	12,425	0.4765	1,713	0.4605	0.4893	3,173
0.3538	12,352	0.5011	1,383	0.4394	0.5128	3,091
0.3580	11,662	0.5236	-953	0.4198	0.5344	2,912
0.3607	9,547	0.5444	-7,061	0.4019	0.5544	2,484
0.3672	7,799	0.5637	-12,290	0.3851	0.5730	1,867
0.7492	14,293	0.5898	-14,451	0.3548	0.6066	585
0.3862	7,303	0.6142	-14,620	0.3410	0.6219	-7

Table 3 (Continued)

Mole dropped, $n_{Cu}$ (mmol)	Heat effect $\Delta H_{signal}$ (J/mol)	Partial enthalpy		Integral enthalpy		
		$x_{Cu}$	$\Delta_{mix}\bar{H}$ (J/mol)	$x_{Bi}$	$x_{Cu}$	$\Delta_{mix}H$ (J/mol)
0.3884	7,233	0.6290	-14,910	0.3282	0.6361	-568
0.3891	7,324	0.6427	-14,705	0.3162	0.6493	-1,082
0.4060	7,800	0.6558	-14,319	0.3047	0.6622	-1,566
0.4163	8,049	0.6683	-14,195	0.2937	0.6744	-2,022
0.4219	8,253	0.6801	-13,970	0.2833	0.6859	-2,444
0.4235	8,384	0.6912	-13,734	0.2736	0.6966	-2,831
Section G, 2nd run, starting amounts: $n(Bi) = 3.3787$ mmol; $n(Sn) = 0.3627$ mmol						
0.3135	16,254	0.0387	18,253	0.8332	0.0773	1,445
0.3413	16,455	0.1131	14,615	0.7686	0.1489	2,467
0.3418	15,468	0.1796	11,658	0.7131	0.2103	3,130
0.3460	14,912	0.2372	9,503	0.6646	0.2641	3,564
0.3549	14,479	0.2881	7,195	0.6212	0.3121	3,801
0.3560	13,989	0.3332	5,695	0.5831	0.3544	3,917
0.3604	13,614	0.3733	4,181	0.5489	0.3922	3,933
0.3681	13,810	0.4093	3,914	0.5179	0.4265	3,932
0.3765	13,621	0.4421	2,580	0.4897	0.4578	3,858
0.3814	13,876	0.4720	2,785	0.4640	0.4862	3,802
0.3859	13,812	0.4991	2,192	0.4407	0.5120	3,721
0.4106	13,600	0.5244	-478	0.4183	0.5368	3,507
0.4116	10,764	0.5481	-7,447	0.3980	0.5593	2,976
0.4286	91,48	0.5699	-12,254	0.3789	0.5805	2,244
0.4352	8,805	0.5902	-13,369	0.3612	0.6000	1,518

Standard states: pure liquid components. Pure Cu dropped into liquid Bi–Sn.

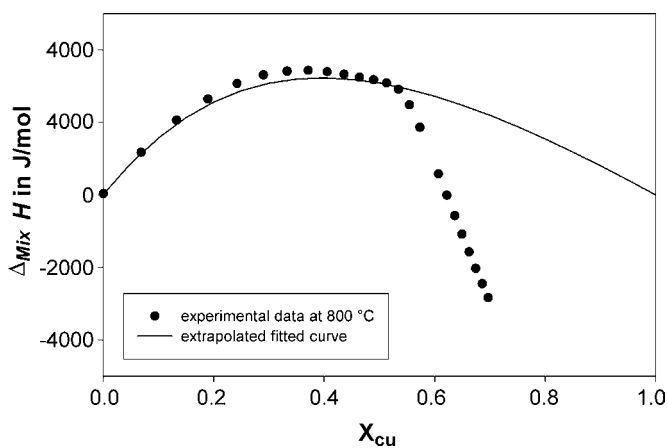


Fig. 3. Integral molar enthalpies of mixing at 800 °C in liquid Bi–Cu–Sn alloys along section G (pure Cu dropped into  $Bi_{0.9}Sn_{0.1}$ ): experimental data and fitted curve; standard states: pure liquid metals.

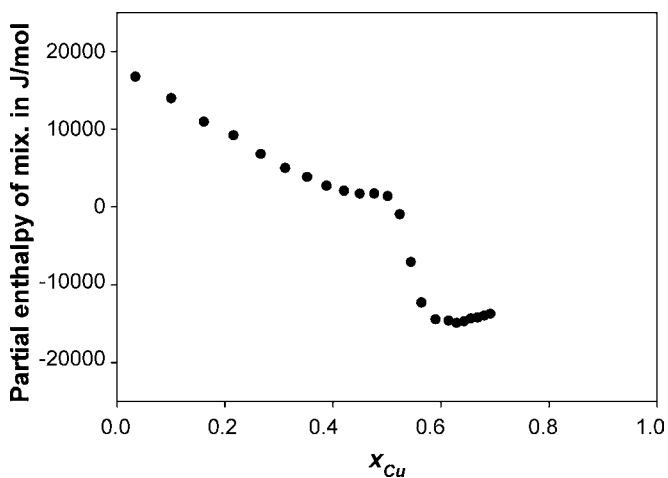


Fig. 4. Partial molar enthalpies of mixing at 800 °C in liquid Bi–Cu–Sn alloys along section G (pure Cu dropped into  $Bi_{0.9}Sn_{0.1}$ ): standard states: pure liquid metals.

primary crystallisation of a solid phase, most probably the (Cu) phase. The rather constant partial values after the occurrence of the solid phase are around  $-14000$  J/mol, see Fig. 4. This is very close to the enthalpy of melting of pure Cu.

4.2. Binary and ternary modeling

In a first step, the experimental data for binary liquid Bi–Cu alloys at 800 and 1000 °C were treated by a least squares fit using the following Redlich–Kister polynomial as proposed by Ansara and

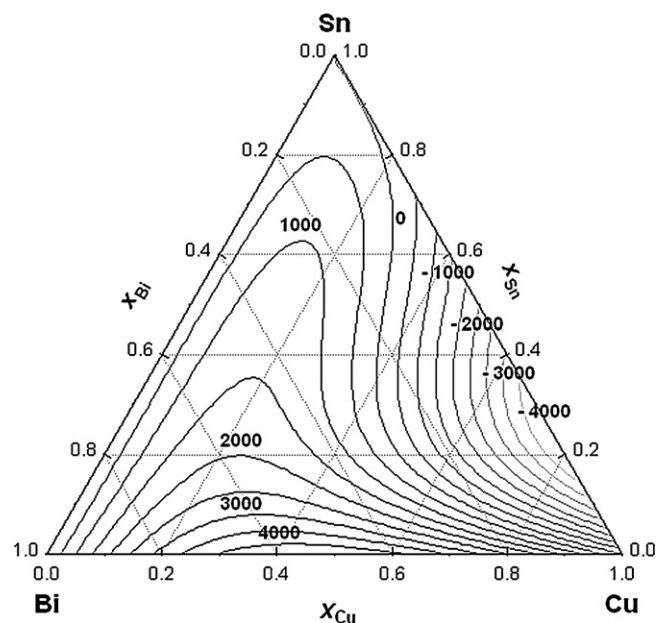


Fig. 5. Integral enthalpy of mixing of liquid Bi–Cu–Sn alloys at 800 °C (in J/mol); standard states: pure liquid metals.



**Table 4**  
Partial and integral enthalpies of liquid Bi–Cu–Sn alloys at 800 °C

Mole dropped, $n_{\text{Cu}}$ (mmol)	Heat effect, $\Delta H_{\text{signal}}$ (J/mol)	Partial enthalpy		Integral enthalpy		
		$x_{\text{Cu}}$	$\Delta_{\text{mix}}\bar{H}$ (J/mol)	$x_{\text{Bi}}$	$x_{\text{Cu}}$	$\Delta_{\text{mix}}H$ (J/mol)
Section H, starting amounts: $n(\text{Bi}) = 0.8999$ mmol; $n(\text{Cu}) = 0.3447$ mmol						
0.2184	5,679	0.0298	–2869	0.8462	0.0596	1,586
0.2542	6,752	0.0902	–2314	0.7913	0.1207	1,333
0.2570	6,904	0.1478	–2011	0.7425	0.1749	1,127
0.2592	7,112	0.1990	–1438	0.6991	0.2231	977
0.2688	7,384	0.2453	–1402	0.6591	0.2675	841
0.5328	14,661	0.3048	–1357	0.5920	0.3421	617
0.2971	8,223	0.3598	–1195	0.5602	0.3774	520
0.3036	8,364	0.3936	–1322	0.5311	0.4098	424
0.3123	8,672	0.4248	–1111	0.5041	0.4398	346
0.3138	8,750	0.4534	–993	0.4796	0.4670	281
0.3151	8,754	0.4794	–1091	0.4573	0.4918	217
0.3266	9,140	0.5035	–893	0.4363	0.5152	166
0.3328	9,372	0.5260	–714	0.4167	0.5369	127
0.3390	9,532	0.5470	–761	0.3986	0.5571	88
0.3392	9,568	0.5664	–668	0.3819	0.5756	56
0.3420	9,479	0.5842	–1160	0.3664	0.5928	7
0.3426	9,595	0.6007	–869	0.3522	0.6086	–27
0.3499	9,808	0.6161	–842	0.3387	0.6236	–58
0.3591	10,173	0.6307	–547	0.3259	0.6378	–77
0.3680	10,474	0.6446	–416	0.3138	0.6513	–89
0.3696	10,499	0.6576	–467	0.3024	0.6639	–103
0.3760	10,659	0.6699	–530	0.2917	0.6758	–118
0.3793	10,743	0.6814	–549	0.2817	0.6870	–133
0.3920	11,062	0.6924	–652	0.2720	0.6978	–151
Section I, starting amounts: $n(\text{Bi}) = 3.1364$ mmol; $n(\text{Cu}) = 1.0732$ mmol						
0.2355	5,554	0.0265	–5318	0.7056	0.0530	3,181
0.2428	5,820	0.0775	–4929	0.6690	0.1020	2,761
0.2539	6,395	0.1251	–3707	0.6347	0.1482	2,429
0.2546	6,556	0.1690	–3152	0.6036	0.1899	2,155
0.4922	12,916	0.2249	–2656	0.5513	0.2600	1,739
0.2643	6,971	0.2764	–2524	0.5269	0.2928	1,550
0.2917	7,865	0.3094	–1932	0.5023	0.3259	1,387
0.3050	8,284	0.3416	–1739	0.4789	0.3573	1,241
0.3178	8,627	0.3721	–1755	0.4567	0.3870	1,103
0.3241	9,035	0.4008	–1022	0.4361	0.4146	1,007
0.3301	9,081	0.4275	–1394	0.4170	0.4403	902
0.3537	9,721	0.4529	–1416	0.3983	0.4655	797
0.3552	9,828	0.4770	–1229	0.3811	0.4885	710
0.3654	9,979	0.4994	–1590	0.3649	0.5103	612
0.3688	10,353	0.5204	–824	0.3499	0.5304	553
0.3710	10,448	0.5398	–741	0.3360	0.5491	502
0.3768	10,673	0.5578	–571	0.3229	0.5666	460
0.3914	10,973	0.5750	–862	0.3104	0.5834	409
0.4065	11,421	0.5914	–802	0.2984	0.5995	362
0.4146	11,712	0.6071	–653	0.2871	0.6147	324
0.4185	11,798	0.6218	–706	0.2765	0.6289	286
0.4226	11,910	0.6356	–715	0.2666	0.6422	250
0.4668	13,219	0.6490	–580	0.2564	0.6559	218
0.4741	13,344	0.6623	–752	0.2468	0.6687	182

Standard states: pure liquid components. Pure Sn dropped into liquid Bi–Cu.

Dupin [38] for substitutional solutions:

$$\Delta_{\text{mix}}H = \sum_i \sum_{j>i} \left[ x_i x_j \sum_{\nu} {}^{(\nu)}L_{i,j} (x_i - x_j)^{\nu} \right] \quad (3)$$

with  $i$  and  $j$  equal to 1 or 2 for the two elements in alphabetical order (1 = Bi and 2 = Cu).  ${}^{(\nu)}L_{ij}$  ( $\nu = 0, 1, 2, \dots$ ) are the corresponding interaction parameters which are listed in Table 5. As the Bi–Cu system shows a nearly regular course of the enthalpy of mixing curves with a maximum close to the equiatomic composition (see Fig. 2), it was sufficient to use only  ${}^{(0)}L$  and  ${}^{(1)}L$  for a perfect fit. The interaction parameters for the two other binary systems which were necessary for the description of the ternary system were calculated based on experimental data from Asryan and Mikula [18] for Bi–Sn and taken from Flandorfer et al. [34] for Cu–Sn.

In a second step, the experimental data for ternary Bi–Cu–Sn alloys were treated by a least squares fit using the following Redlich–Kister–Muggianu polynomial [39] which takes also additional ternary interactions into account:

$$\Delta_{\text{mix}}H = \sum_i \sum_{j>i} \left[ x_i x_j \sum_{\nu} {}^{(\nu)}L_{i,j} (x_i - x_j)^{\nu} \right] + x_1 x_2 x_3 ({}^{(0)}M_{1,2,3} x_1 + {}^{(1)}M_{1,2,3} x_2 + {}^{(2)}M_{1,2,3} x_3) \quad (4)$$

with  $i$  and  $j$  equal to 1, 2, and 3 for the elements Bi, Cu, and Sn, respectively.  ${}^{(\nu)}L_{ij}$  ( $\nu = 0, 1, 2, \dots$ ) are the interaction parameters of the constituent binaries which were taken from Table 5. The last term represents the additional mixing enthalpy due to ternary interactions where  ${}^{(\alpha)}M_{1,2,3}$  ( $\alpha = 0, 1, 2$ ) are the excess ternary interaction parameters. The results for the ternary interaction parameters

**Table 5**  
Binary and ternary interaction parameters in the liquid Bi–Cu–Sn system

Interaction parameter	$T$ (°C)	$\nu, \alpha$	J/mol
${}^{(v)}L_{\text{Bi,Sn}}^a$	450	0	442
		1	–298
${}^{(v)}L_{\text{Bi,Cu}}$	800	0	17,810
		1	3,331
	1000	0	20,797
		1	–1,225
${}^{(v)}L_{\text{Cu,Sn}}$ [34] <sup>b</sup>	800	0	–9,857
		1	–22,755
		2	–13,424
${}^{(\alpha)}M_{\text{Bi,Cu,Sn}}$	800	0	5,808
		1	–67,614
		2	51,555

<sup>a</sup> Derived from data given in Ref. [18].

<sup>b</sup> Mean value of parameters given for 900 and 1100 °C in Ref. [34].

**Table 6**  
Values of the enthalpy of mixing at the intersection points of Cu-additions and Sn-additions (grey shaded)

Molar concentrations			Sections with $\Delta_{\text{Mix}}H$ values at intersections in J/mol						
$x_{\text{Bi}}$	$x_{\text{Cu}}$	$x_{\text{Sn}}$	C	D	E	F	G	H	I
0.69	0.23	0.08					3,085		2,963
0.82	0.09	0.09					1,555	1,597	
0.60	0.20	0.20				2,556			2131
0.69	0.08	0.23				1222		1075	
0.54	0.18	0.28			2,000				1657
0.61	0.07	0.32			889			785	
0.42	0.15	0.43		1,222					941
0.48	0.05	0.47		556				379	
0.30	0.10	0.60	654						404
0.32	0.04	0.64	278					36	

${}^{(\alpha)}M_{\text{Bi,Cu,Sn}}$  are included in Table 5. Finally, Eq. (4) was used to calculate the enthalpy of mixing of liquid Bi–Cu–Sn alloys at 800 °C over the entire composition range, and the outcome is shown in Fig. 5 as a ternary contour plot. Note that the values in the copper-rich corner refer to the metastable liquid alloy since the liquidus temperatures are higher than 800 °C in this composition range. The values of the integral enthalpy of mixing at the intersection points of Cu-additions and Sn-additions are given in Table 6.

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