# Bismuth – Indium – Tin

*Olga Fabrichnaya, Viktor Witusiewicz, Joachim Gröbner*

### Introduction

The ternary Bi-In-Sn system was investigated for potential lead-free low-melting solder. First experimental work on this system using X-ray and microscopy methods was published by [1964Doo] follwed by experiments performed by [1967Sch]. Applying thermal, metallographic and X-ray analysis they found the temperature and liquid composition of an eutectic reaction involving (Sn), (Bi) and InBi. [1972Ste1] and [1972Ste2] studied 7 polythermal sections inside the In-InBi-Sn region using differential thermal analysis and X-ray diffraction. [1984Kab] found a eutectic at 59°C involving the phases $In_2Bi$, γ, and β. They solidified the alloys directionally and characterized them by metallographic methods. In [1986Kab] the section $In_2Bi$-Sn was investigated and a projection of the liquidus surface is given. Specimens of eutectic Bi-InBi-γ at 77°C were unidirectionally solidified at very low speed and quenched to form a representative solid/liquid interface in the study of [1995Rug]. Precipitates observed in the InBi phase showed some solubility of Bi and Sn at the ternary eutectic temperature.
In their review of low-temperature solders [1994Mei] showed a liquidus surface based on an unpublished work of Choongun Kim and J.W. Morris (Universtiy of California at Berkeley). The same diagram is given by [1997Hua]. [1999Yoo] investigated the ternary system by X-ray diffraction, energy-dispersive X-ray spectroscopy, optical and scanning electron microscopy. They compared 14 vertical sections with their own results and with those of [1964Doo], [1972Ste2], [1986Kab] and [1967Sch]. In the recent investigation of [2005Wit] measurements of enthalpy of melting were performed on 28 alloys by differential scanning calorimetry (DSC). The tie triangle (Bi)-InBi-(Sn) at 77°C, tie triangle $In_2Bi$-β-γ and tie line $In_2Bi$-γ at 59°C and composition of liquid at eutectic at 59°C were measured using unidirectionally solidified samples which were derived from extremely slow pulling velocity and measured by energy and wavelength dispersive X-ray analysis (EDX and WDX). It was demonstrated that β and γ phase could dissolve up to 11.4 and 21.2 at.% Sn, respectively
A complete thermodynamic calculation of the ternary system is given by [1999Yoo, 2000Ohn, 2002Moe, 2003Moe, 2005Wit]. The mentioned assessments produce different liquidus surface. A summary of the experimental work can be found in [1999Yoo].

### Binary Systems

All three edge binary phase diagrams are in this evaluation accepted from [2002Moe, 2003Moe]. These systems are virtually equivalent to those of [Mas2].

### Solid Phases

The crystallographic data of the phases in the Bi-In-Sn system and their ranges of stability are listed in Table 1.

### Quasibinary Systems

[1964Doo] constructed a simple eutectic section between InBi and Sn and assumed a quasibinary which divided the ternary phase diagram in two sections. [1997Hua] reported the eutectic temperature of this quasibinary section as 82°C. [1986Kab] concidered also the $In_2Bi$ - Sn section to be a quasibinary phase diagram. [1999Yoo] showed that both sections are not quasibinary.

### Invariant Equilibria

The temperatures of the invariant reactions are listed in Table 2 along with phase composition. Those reactions which involve the liquid phase were calculated using the data sets developed by [2005Wit]. The reaction scheme, following from this calculation is given in Fig. 1. In general, the calculated temperatures and compositions of invariant reactions approach the experimental values, even though the type of the reactions and the involved phases are different in some cases. It should be mentioned that the experimental works of [1967Sch, 1972Ste1, 1986Kab, 1999Yoo] are also mutually inconsistent regarding the phases and their nature. In the study of [2005Wit] the type and phases involved in $E_2$ and $U_3$ were experimentally verified.

### Liquidus, Solidus and Solvus Surfaces

[1967Sch], [1986Kab] and [1994Mei] showed an experimentally derived liquidus surface. The first calculated liquidus surface is given by [1999Yoo]. However, in this calculation the β phase ($In_9Bi$) was missing. The liquidus projection presented in Fig. 2 is taken from yet unpublished calculations made by [2005Wit].

### Isothermal Sections

The isothermal sections at 76.45, 59.5 and 25°C were studied experimentally and calculated by [2005Wit], they are presented in Figs. 3, 4 and 5, respectively.

### Temperature – Composition Sections

[1999Yoo] calculated 14 vertical sections and presented them along with the experimental metallurgical data measured by [1964Doo, 1972Ste2, 1986Kab, 1999Yoo]. [2005Wit] calculated 14 vertical sections at the same conditions as [1999Yoo] and 3 sections which were also studied experimentally. Figures 6 to 10 present 5 of those calculated vertical sections. The selected diagrams represent most of the experimentally studied sections, but the (βSn)/(αSn) transformation is not taken into account.

### Thermodynamics

The first thermodynamic calculation of the whole ternary system, describing the Gibbs energies of all phases by the Calphad method was reported by [1999Yoo]. However, no experimentally measured thermodynamic data were available at that time. The only experimental thermodynamic data for the Bi-In-Sn system became available later in [2005Wit]. They are enthalpies of melting for 28 alloys measured by DSC technique. These enthalpies of the $E_1$ and $E_2$ invariant reactions are given in Table 3 as calculated from the thermodynamic database of [2005Wit], in a very good agreement with the DSC measurements. [2005Wit] gives a new data set for the ternary system considering the β phase ($In_9Bi$), which is in better agreement with the experimental data than the earlier calculation. The underlying data set was derived using all available data on phase relations and the experimentally determined enthalpies of melting. This is why many of the data and diagrams from that work have been included here.

### Notes on Materials Properties and Applications

The lead - tin solder alloys are still commonly used. However there is growing need to develop Pb free solder alloys less damaging for the environment [1999Yoo, 2000Ohn, 2003Moe]. Several Pb free alloys with relatively low melting point have been considered [1999Ohn1, 1999Ohn2, 2000Ohn, 2003Moe]. A candidate lead free solder alloy must fulfill many requirements: wettability of the substrate, ability to form a strong chemical bond with the substrate, suitable melting and solidification behavior, good mechanical properties, corrosion resistance, electrical conductivity and it must not be harmful to health and environment [2003Moe]. The Bi-In-Sn alloys are among the most promising Pb free solders.

[2002Wan] predicts the viscosity of the ternary Bi-In-Sn melt based on Seetharaman's viscosity model and Chou's geometric-thermodynamic model. The viscosity at 500 and 600°C is given for the ratio $x_{Bi}/x_{In} = 1$. Solute diffusion coefficients in the Bi-In-Sn system were measured in microgravity by [2004Gar], using the shear cell technique.

The microstructure and properties of a Bi-In-Sn eutectic alloy was studied in [2002Sen]. A ternary eutectic alloy obtained by continuous casting has more uniform microstructure contrary to the heavily segregated structure of the statically cast specimens. These differences in structure significantly affected the mechanical properties. Contrary to the statically cast specimens wires from continuous casting do exhibit a considerable ductility.

## References

[1964Doo] Dooley, G.J., Peretti, E.A., "Phase Diagram of the System InBi-Sn", *J. Chem. Eng. Data*, **9**, 90-91 (1964) (Experimental, #, 0)

[1967Sch] Scherpereel, L.R., Peretti, E.A., "The Ternary Subsystem Indium Bismuthide-Bismuth-Tin", *J. Mater. Sci*., **2**, 256-259 (1967) (Experimental, Phase Diagram, #, 2)

[1972Ste1] Stelmakh, S.I., Tsimmergakl, V.A., Sheka, I.A., "The In-Sn-InBi System", *Ukr. Khim. Zh*., **38**, 855-859 (1972) (Experimental, #, 13)

[1972Ste2] Stelmakh, S.I., Tsimmergakl, V.A., Sheka, I.A., "The Compound $In_2Bi$", *Progr. Sov. Chem*., **38**, 631-633 (1972) (Experimental, #, 9)

[1984Kab] Kabassis, H., Rutter, J.W., Winegard, W.C., "Microstructure of One of the Ternary Eutectic Alloys in the Bi-In-Sn System", *Metall. Trans. A*, **15A**, 1515-1517 (1984) (Experimental, Morphology, 12)

[1986Kab] Kabassis, H., Rutter, J.W., Winegard, W.C., "Phase Relationships in Bi-In-Sn Alloy System", *Mater. Sci. Technol*., **2**, 985-988 (1986) (Experimental, Phase Diagram, 8)

[1994Mei] Mei, Z, Vander Plas, H., Gleason, J., Baker, J., "Low-Temperature Solders", *Proc. Electronic Mater. Proces. Symp. Nov. 13-18*, 485-495 (1994) (Review, Phase Diagram, #, 33)

[1995Rug] Ruggiero, M.A., Rutter, J.W., "Origing of Microstructure in 350 K Eutectic of Bi-In-Sn Ternay System", *Mater. Sci. Technol.*, **11**(2), 136-142 (1995) (Experimental, Phase Relations, 22)

[1997Hua] Hua, F., Glazer, J., "Lead-Free Solders For Electronic Assembly", *Des. Reliab. Solders Solder Interconnect.*, Proc. Symp., 65-73 (1997) (Review, #, 63)

[1999Ohn1] Ohnuma, I., Liu, X.J., Ohtani, H., Ishida, K., "Thermodynamic Database for Phase Diagrams in Micro-Soldering Alloys", *J. Electron. Mater*., **28**(11), 1164-1171 (1999) (Calculation, Phase Relations, 22)

[1999Ohn2] Ohnuma, I., Liu, X.J., Ohtani, H., Ishida, K., "Phase Diagrams of Pb-Free Solder Alloys" (in Japanese), *Materia Japan*, **38**, 923-926 (1999) (Calculation, Phase Diagram, Phase Relations, 13)

[1999Yoo] Yoon, S.W., Rho, B.-S., Lee, H.M., Kim, C.-U., Lee, B.-J., "Investigation of the Phase Equilibria in the Sn-Bi-In Alloy System", *Metall. Mater. Trans. A*, **30A**, 1503-1515 (1999) (Experimental, Calculation, Phase Relations, #, *, 17)

[2000Ohn] Ohnuma, I., Cui, Y., Liu, X.J., Inohana, Y., Ishihara, S., Ohtani, H., Kainuma, R., Ishida, K., "Phase Equilibria of Sn-In Based Micro-Soldering Alloys", *J. Electron. Mater*., **29**(10), 1113-1121 (2000) (Calculation, Phase Diagram, Phase Relations, Thermodyn., 27)

[2002Moe] Moelans, N., *"Calculation of Phase Diagram for Lead-free Solder Alloys Based on Bi-In-Sn-Zn System"* (in Dutch), Ph.D. Thesis, Catholic University of Leuven, Leuven, Belgium (2002) (Calculation, Phase Diagram, Phase Relations, Thermodyn., 44)

[2002Sen] Sengupta, S., Soda, H., McLean, A., "Microstructure and Properties of a Bismuth-Indium-Tin Eutectic Alloy", *J. Mater. Sci.*, **37**, 1747-1758 (2002) (Experimental, Mechan. Prop., Morphology, 12)

[2002Wan] Wang, X., Bao, H., Li, W., "Estimation of Viscosity of Ternary-Metallic Melts", *Metall. Mater. Trans. A*, **33**(10), 3201-3204 (2002) (Calculation, Phys. Prop., 18)

[2003Moe] Moelans, N, Hari Kumar, K.C, Wollants, P., "Thermodynamic Optimization of the Lead-Free Solder System Bi-In-Sn-Zn", *J. Alloys Compd.,* **360**, 98-106 (2003) (Calculation, Phase Diagram, Phase Relations, Thermodyn., 44)
[2004Gar] Garandet, J.P., Mathiak, G., Botton, V., Lehmann, P., Griesche, A., "Reference Microgravity Measurements of Liquid Phase Solute Diffusivities in Tin- and Aluminum-Based Alloys", *Int. J. Thermophys*., **25**(1), 249-272 (2004) (Experimental, Transport Phenomena, 43)
[2005Wit] Witusiewicz, V.T., Hecht, U., Boettger, B., Rex, S., "Thermodynamic Re-Optimisation of the Bi-In-Sn System on the Basis of New Experimental Data", to be submitted (Experimental, Calculation, Phase Diagram, Phase Relations, Thermodyn., 23)

**Table 1:** Crystallographic Data of Solid Phases

| Phase/<br>Temperature Range<br>[°C] | Pearson Symbol/<br>Space Group/<br>Prototype | Lattice Parameters<br>[pm] | Comments/References |
|---|---|---|---|
| (Bi)<br>< 271.442 | *hR*6<br>$R\bar{3}m$<br>As | *a* = 454.613<br>*c* = 1186.152 | at 31°C [V-C2]<br>~ 0 at.% In |
| (In)<br>< 156.63 | *tI*2<br>*I*4/*mmm*<br>In | <br>*a* = 325.3<br>*c* = 494.70 | 0 to 8 at.% Bi [Mas2]<br>pure In |
| (βSn)<br>293.9681 - 13 | *tI*4<br>$I4_1/amd$<br>Sn | <br>*a* = 583.16<br>*c* = 318.15 | 0 to 13.1 at.% Bi, [Mas2]<br>pure Sn |
| (αSn) (l)<br>< 13 | *cF*8<br>$Fd\bar{3}m$<br>C (diamond) | *a* = 648.92 | at 25°C [Mas2] |
| InBi<br>< 110.0 | *tP*4<br>*P*4/*nmm*<br>PbO | *a* = 501.5<br>*c* = 477.1 | [V-C2, Mas2] |
| $In_5Bi_3$<br>< 88.9 | *tI*32<br>*I*4/*mcm*<br>$Cr_5B_3$ | *a* = 846 to 854<br>*c* = 1256 to 1268 | 62.2 to 62.66 at.% In<br>[V-C2, Mas2] |
| $In_2Bi$<br>< 89.5 | *hP*6<br>$P6_3/mmc$<br>$Ni_2In$ | *a* = 549.6<br>*c* = 657.9 | 66.8 to 67.7 at.% In<br>[V-C2, Mas2] |
| β, $In_{9-x}Sn_xBi$<br>$In_9Bi$<br>93.5 - 49<br><br><br>$In_{1-x}Sn_x$<br>~140- ~–133 | *tI*2<br>*I*4/*mmm*<br>In | <br>*a* = 347.2<br>*c* = 449.5<br><br><br>*a* = 345.9<br>*c* = 439.7 | <br>88 to 92 at.% In<br>[Mas2]<br>at 90 at.% In and 70°C [V-C2]<br>12 < *x* < 44 at.% Sn<br>at *x* = 25 at.% Sn<br>[Mas2, V-C2] |
| γ, $In_{1-x}Sn_x$<br>< 224 | *hP*1<br>*P*6/*mmm*<br>InBi | *a* = 320.8<br>*c* = 299.7 | 72 < *x* < 98 at.% Sn<br>at *x* = 80 at.% Sn<br>[Mas2, V-C2] |

**Table 2:** Invariant Equilibria

| Reaction | *T* [°C] | Type | Phase | Composition (at.%) | | |
|---|---|---|---|---|---|---|
| | | | | Bi | In | Sn |
| L ⇌ (βSn) + InBi | 76.54 | $e_5$(max) | L | 38.0 | 37.2 | 24.8 |
| | | | (βSn) | 25.4 | 23.4 | 51.2 |
| | | | InBi | 49.3 | 50.0 | 0.7 |
| L ⇌ (Bi) + (βSn) + InBi | 76.40 | $E_1$ | L | 39.3 | 36.0 | 24.7 |
| | | | (Bi) | 99.9 | 0.00 | 0.01 |
| | | | (βSn) | 26.1 | 22.9 | 51.0 |
| | | | InBi | 49.4 | 50.0 | 0.6 |
| L + (βSn) ⇌ γ+ InBi | 76.25 | $U_1$ | L | 35.7 | 37.6 | 25.0 |
| | | | (βSn) | 24.1 | 24.3 | 51.6 |
| | | | γ | 9.1 | 23.2 | 67.7 |
| | | | InBi | 49.3 | 50.0 | 0.7 |
| L + InBi ⇌ γ + $In_5Bi_3$ | 62.26 | $U_2$ | L | 24.4 | 57.8 | 17.8 |
| | | | InBi | 48.9 | 50.0 | 1.1 |
| | | | γ | 21.7 | 43.2 | 35.1 |
| | | | $In_5Bi_3$ | 36.6 | 62.5 | 0.9 |
| L + $In_5Bi_3$ ⇌ γ + $In_2Bi$ | 61.50 | $U_3$ | L | 23.6 | 58.4 | 18.0 |
| | | | $In_5Bi_3$ | 36.6 | 62.5 | 0.9 |
| | | | γ | 20.9 | 43.0 | 36.1 |
| | | | $In_2Bi$ | 32.2 | 66.7 | 1.1 |
| L ⇌ γ + β + $In_2Bi$ | 59.28 | $E_2$ | L | 20.7 | 60.2 | 19.1 |
| | | | γ | 16.3 | 40.4 | 43.3 |
| | | | β | 8.8 | 66.8 | 24.4 |
| | | | $In_2Bi$ | 32.0 | 66.7 | 13.1 |

**Table 3:** Thermodynamic Data of Reaction or Transformation

| Reaction or Transformation | *T* [°C] | Quantity, per mol of atoms [kJ, mol, K] | Comments |
|---|---|---|---|
| 0.477(Sn)+0.5016$In_{0.5}Bi_{0.5}$+0.021(Bi) = $In_{0.3599}Sn_{0.2467}Bi_{0.3933}$ (Liq) | 76.40 | Δ*H* = 5149 | [2005Wit] calculation + DSC |
| 0.4313 $In_{0.667}Bi_{0.333}$ + 0.321β + 0.2473γ = $In_{0.6021}Sn_{0.1912}Bi_{0.2067}$ (Liq) | 59.28 | Δ*H* = 3478 | [2005Wit] calculation + DSC |

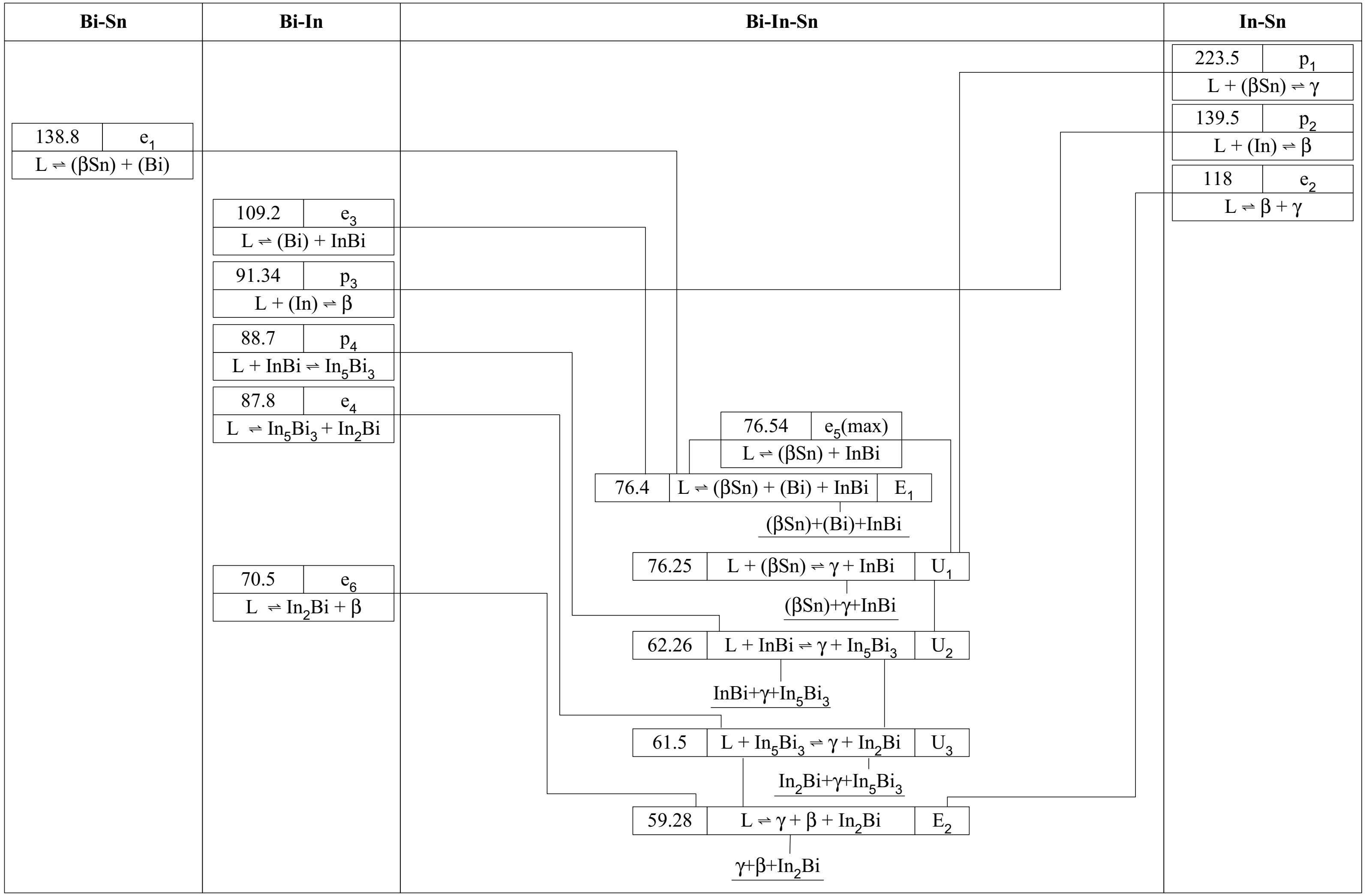


**Fig. 1: Bi-In-Sn.** Reaction scheme

**Fig. 2: Bi-In-Sn.** Liquidus surface projection

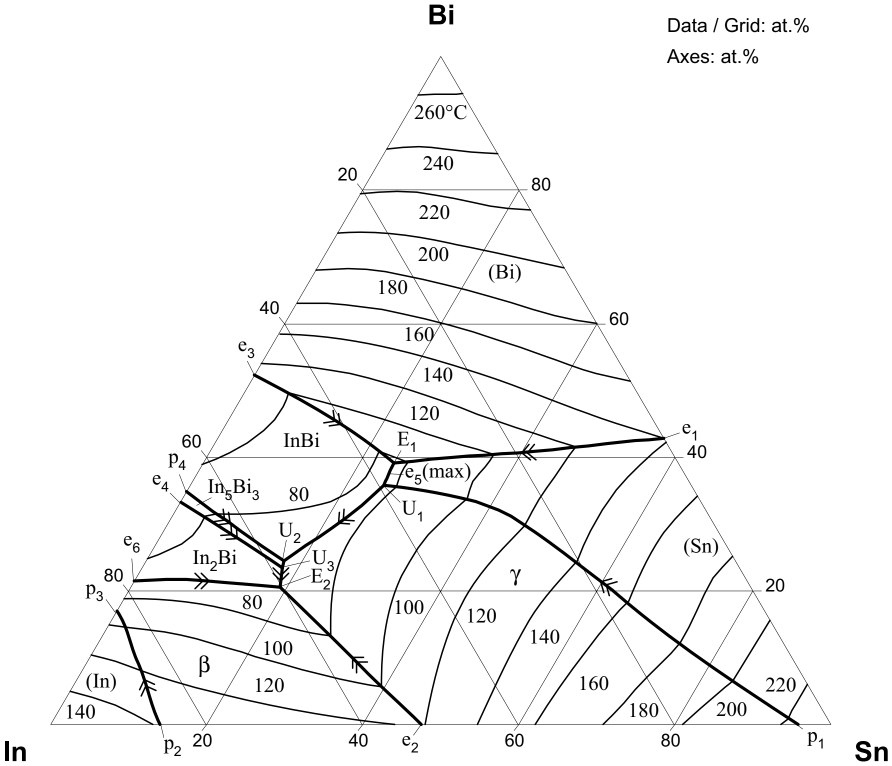


**Fig. 3: Bi-In-Sn.** Isothermal section at 76.45°C

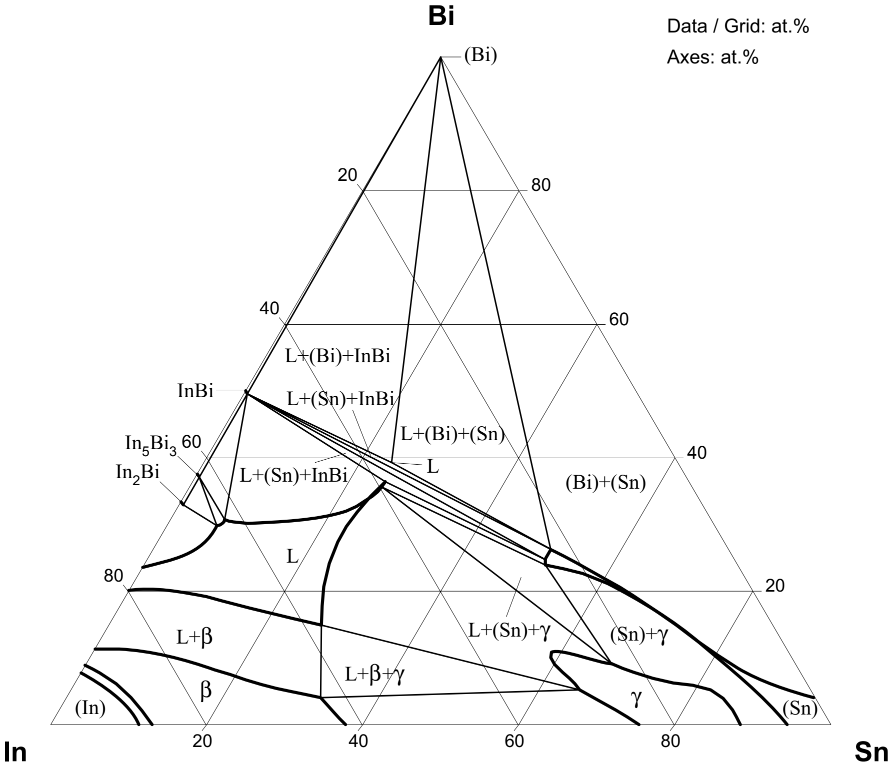

**Fig. 4: Bi-In-Sn.** Isothermal section at 59.5°C

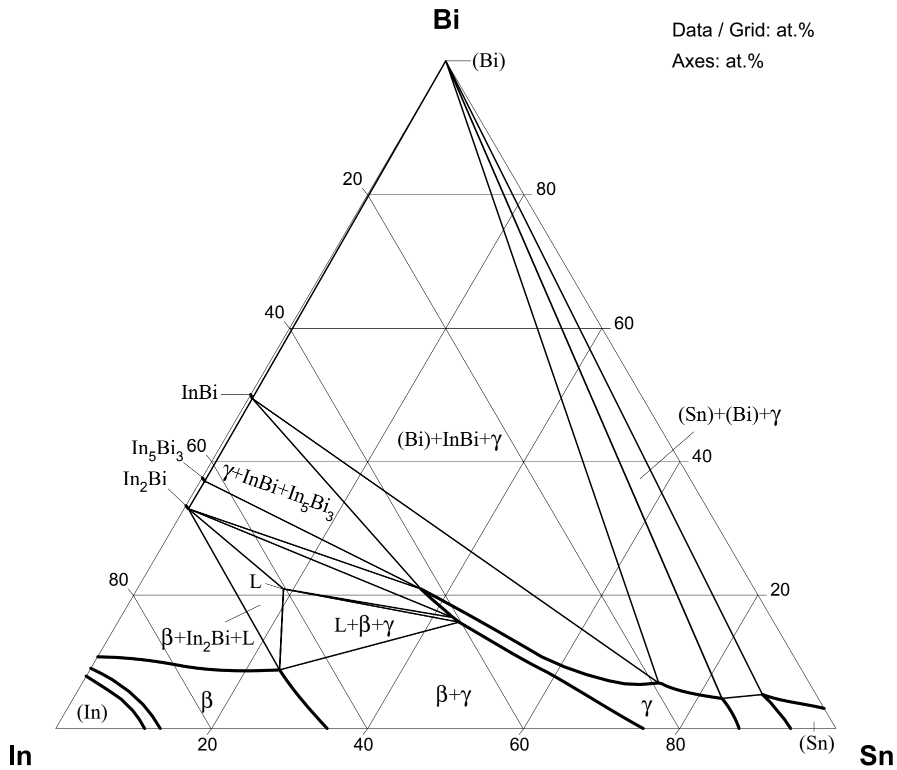


**Fig. 5: Bi-In-Sn.** Isothermal section at 25°C

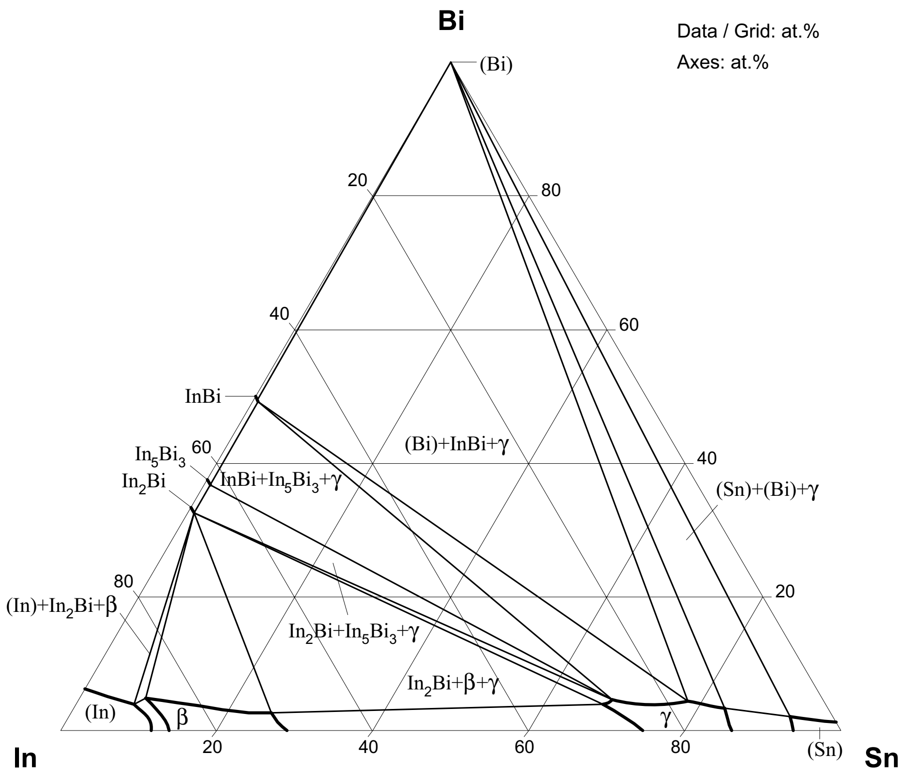

**Fig. 6: Bi-In-Sn.** Vertical section at mass ratio Bi/In=95/5, plotted in at.%

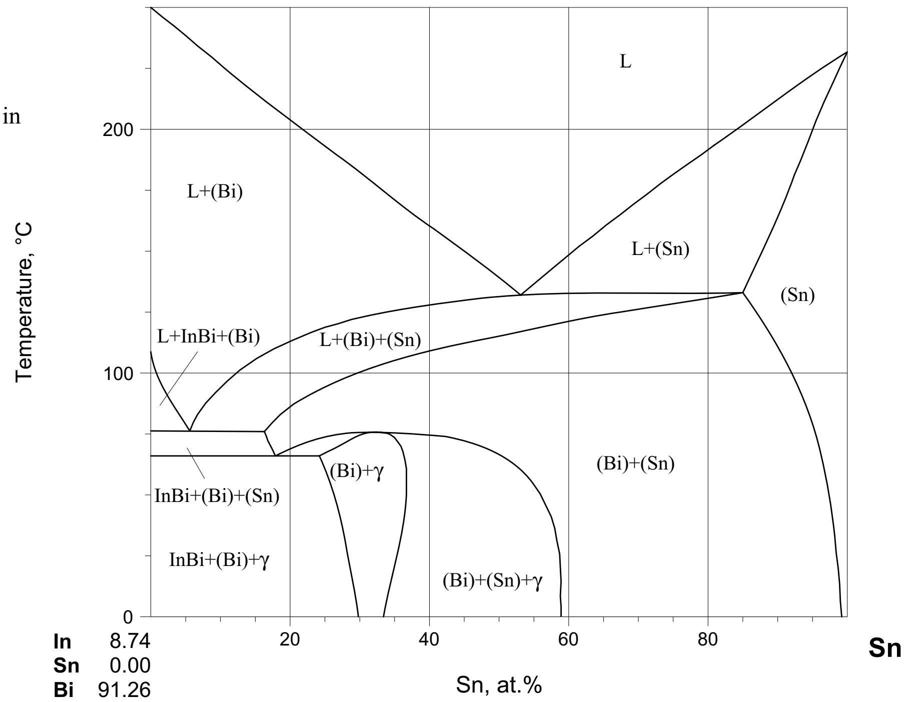


**Fig. 7: Bi-In-Sn.** Vertical section at 50 mass% Sn, plotted in at.%

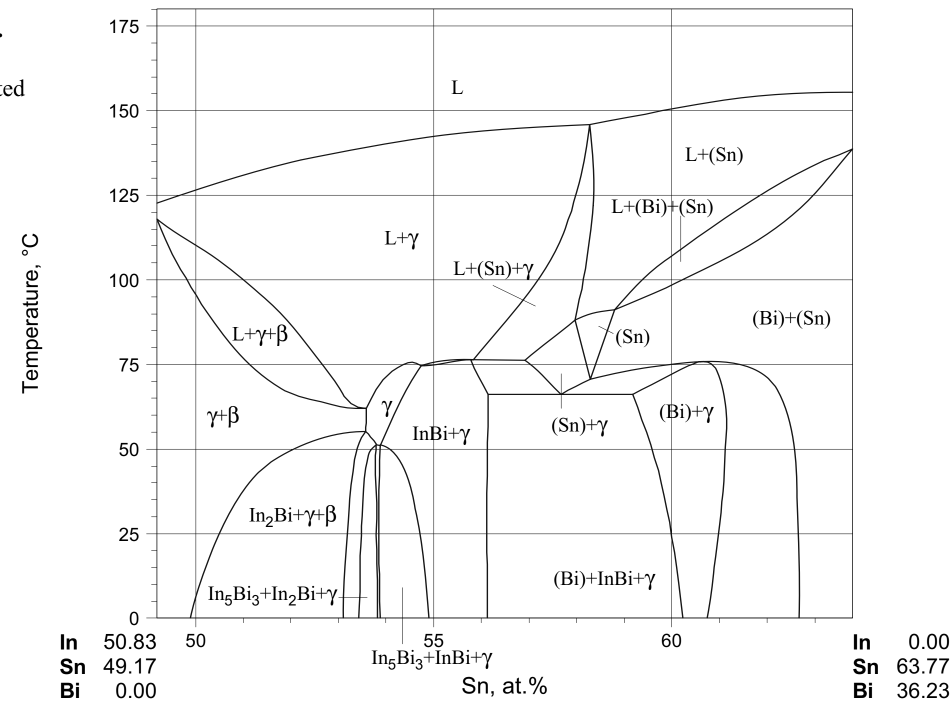

**Fig. 8: Bi-In-Sn.** Vertical section at mass ratio Sn/Bi=30/70, plotted in at.%

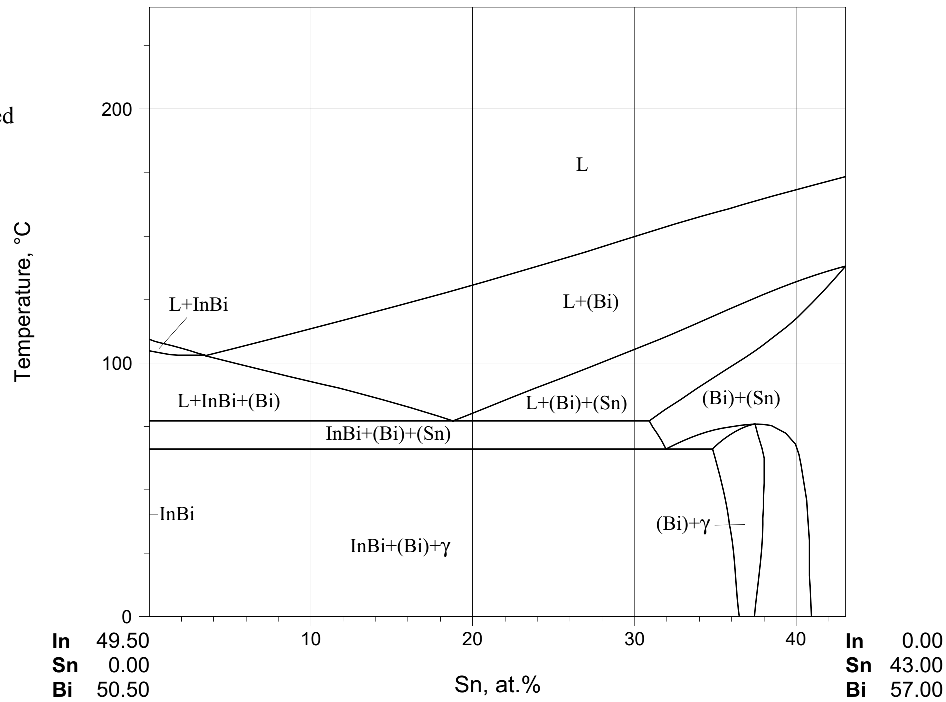


**Fig. 9: Bi-In-Sn.** Vertical section InBi-Sn

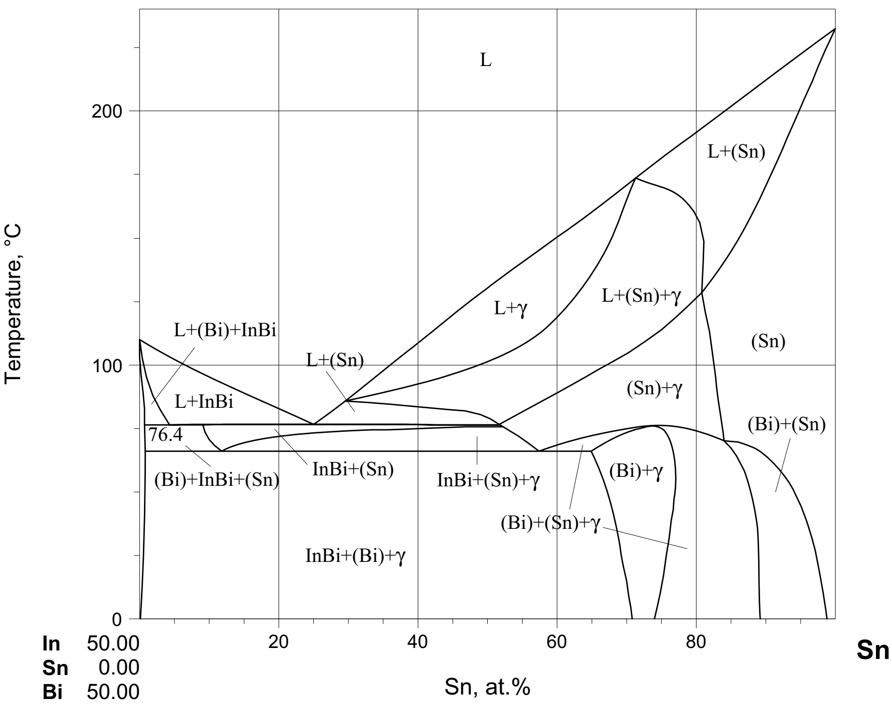

**Fig. 10: Bi-In-Sn.** Vertical section $In_2Bi$-Sn, plotted in at.%