



Thermodynamics and phase diagram calculation of some sections in the Ag–Bi–Sn system

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Abstract: The thermodynamic properties and characteristic phase diagrams of some sections in the Ag–Bi–Sn system were calculated. The thermodynamic functions, such as Gibbs excess energy, activity and enthalpy of formation, were calculated using the RKM model and compared with experimental data reported in the literature. Iso-activity diagrams for all three components at 900 K have been constructed. The calculated phase diagrams of the vertical sections Sn–AgBi, Ag–BiSn and Bi–AgSn, obtained using the ThermoCalc program, were compared and confirmed with the results of DTA measurements from the present work.

Keywords: thermodynamics, phase diagrams, ternary alloys, Ag–Bi–Sn system, lead-free solders.

INTRODUCTION

Although originally commenced as an environmental issue, lead-free soldering is rapidly evolving into an important issue for the worldwide electronic industry.^{1,2} A contribution to this topic at the European level has been given in the frame of the COST 531 Action “Lead-free solder materials”,³ during which, based on a recent version 4.4 SGTE,⁴ a new thermodynamic database for lead-free solder alloys was developed.⁵ It also contains data for carefully tested binary phase diagrams, suitable for the prediction of phase equilibria in multicomponent solder systems.

Among the lead-free solder alternatives for surface mount assembly, systems based on Ag–Sn were considered as the most promising. Especially the Ag–Bi–Sn system was determined to be a very applicable one, since its solderability was positively assessed among a range of lead-free alloys.²

Considering the thermodynamic description of the Ag–Bi–Sn system, there are few papers dealing with experimental investigations of thermodynamics properties of the ternary Ag–Bi–Sn system. Hassam *et al.*⁶ determined mixing enthal-

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pies of liquid alloys by direct reaction calorimetry. Recently, Katayama *et al.*⁷ measured activities of tin using the fused salt EMF method.

A thermodynamic optimization of the Ag–Bi–Sn ternary system, was performed by Zabdyr *et al.*,⁵ while a phase equilibria investigation of this system was presented by Ohtani *et al.*,⁸ who established that the investigated system includes three ternary invariant reactions – two ternary transitory peritectics at 263.6 °C and 262.5 °C, and one ternary eutectic at 139.2 °C.

In this work, the results of a calculation of the thermodynamic properties and phase diagram in the chosen sections of the Ag–Bi–Sn system are compared with experimental DTA data, from this work and the literature, as a contribution to more complete comprehension of the thermodynamics and phase equilibria of this ternary system.

Theoretical fundamentals

The Gibbs energies of liquid and substitutional solid phases in ternary system are described by the sub-regular solution model with the Redlich–Kister–Muggianu model⁹ as follows:

$$G_m^\phi = \sum_{i=1}^3 x_i^\phi G_i^\phi + RT \sum_{i=1}^3 x_i^\phi \ln x_i^\phi + G^E(T, x_2) \quad (1)$$

$$G^E(T, x_2) = x_1^\phi x_2^\phi L_{1,2}^\phi + x_2^\phi x_3^\phi L_{2,3}^\phi + x_3^\phi x_1^\phi L_{1,3}^\phi + x_1^\phi x_2^\phi x_3^\phi L_{1,2,3}^\phi \quad (2)$$

where $L_{1,2}^\phi, L_{2,3}^\phi, L_{1,3}^\phi$ are binary temperature-dependent interaction parameters, and $L_{1,2,3}^\phi$ presents the ternary interaction parameter, expressed in the form:

$$L_{1,2,3}^\phi = x_1 L_{123}^0 + x_2 L_{123}^1 + x_3 L_{123}^2 \quad (3)$$

and optimized on the basis of the available thermodynamic and phase diagram data.

EXPERIMENTAL

Alloys of the Ag–Bi–Sn system were prepared from the pure metals (99.999 %) by melting together weighed amounts of tin, silver and bismuth in evacuated and sealed quartz tubes. After melting, the samples were annealed at 300 °C for 200 h and slowly cooled inside the furnace to room temperature.

The DTA measurements were performed using a Derivatograph (MOM Budapest) apparatus equipped with a Pt/Pt 10 % Rh thermocouples under the following conditions: air atmosphere, heating rate 5 K min⁻¹ using sintered Al₂O₃ as the reference specimen.

RESULTS AND DISCUSSION

Starting data

The basic data for the calculation of the thermodynamic properties and the phase diagrams were the optimized thermodynamic parameters for the Ag–Bi–Sn system compiled elsewhere,⁵ including all binary subsystems, *i.e.*, Ag–Sn,¹⁰ Ag–Bi^{11,12} and Bi–Sn.^{13,14}

The pure solid elements at 298.15 K and 1 bar in their stable form were chosen as the reference state for the systems (SER) and, therefore, Version 4.4 of the

SGTE Unary Database (Scientific Group Thermodata Europe) of the phase stabilities for the stable and metastable states of pure elements² was employed.

The following phases from the constitutive binary subsystems, considered in the COST 531 Database⁵ and presented in Table I, were used in the calculations in this work: liquid phase, the Sn-rich bct phase (denoted as BCT_A5), the Ag-rich fcc phase (denoted as FCC_A1), the Bi-rich rhombohedral phase (denoted as RHOMBOHEDRAL_A7), the orthorhombic order structure Ag₃Sn (denoted as AGSB_ORTHO) and the hcp phase (denoted as HCP_A3).

TABLE I. Optimized thermodynamic parameters for the Sn–Ag–Bi ternary system from the literature⁵

LIQUID	
EXCESS MODEL IS REDLICH-KISTER_MUGGIANU	
CONSTITUENTS: AG,BI,SN	
L(LIQUID,AG,BI;0)	=+3340.81+39.16749*T-5.969876*T*LN(T)
L(LIQUID,AG,BI;1)	= -5485.45-1.07133*T
L(LIQUID,AG,BI;2)	= -3055.34+1.77449*T
L(LIQUID,AG,SN;0)	= -399.49-31.42004*T+3.081837*T*LN(T)
L(LIQUID,AG,SN;1)	= -18150.65+5.87501*T
L(LIQUID,AG,SN;2)	= -12009.03+5.18355*T
L(LIQUID,BI,SN;0)	=+500+1.5*T
L(LIQUID,BI,SN;1)	=-100-0.135*T
L(LIQUID,AG,BI,SN;0)	= +4093.27+63.407508*T
L(LIQUID,AG,BI,SN;1)	= +11188.52-8.978544*T
L(LIQUID,AG,BI,SN;2)	=+17072.3-21.742545*T
AGSB_ORTHO	
2 SUBLATTICES, SITES .75: .25	
CONSTITUENTS: AG : AG,BI,SN	
G(AGSB_ORTHO,AG:AG;0)	=H298(FCC_A1,AG;0) =+GHSERAG+4750-0.5*T (298.14<T< 3000.00)
G(AGSB_ORTHO,AG:BI;0)	=-0.75 H298(FCC_A1,AG;0)-0.25 H298(RHOMBOHEDRAL_A7,BI;0) =+0.75*GHSERAG+0.25*GHSERBI+5 (298.14<T< 3000.00)
G(AGSB_ORTHO,AG:SN;0)	=-0.75 H298(FCC_A1,AG;0)-0.25 H298(BCT_A5,SN;0) = -11085.3+110.01471*T-23.18*T*LN(T)-0.00359*T ² +4389.5*T ⁽⁻¹⁾
L(AGSB_ORTHO,AG:AG,BI;0)	= 0.0
L(AGSB_ORTHO,AG:AG,SN;0)	= 0.0
L(AGSB_ORTHO,AG:BI,SN;0)	= -1000
FCC_A1	
2 SUBLATTICES, SITES 1: 1	
CONSTITUENTS: AG,BI,SN : VA	
L(FCC_A1,AG,BI:VA;0)	=+25077.78-12.05475*T
L(FCC_A1,AG,SN:VA;0)	= +745.45+11.498027*T
L(FCC_A1,AG,SN:VA;1)	= -36541.5
L(FCC_A1,BI,SN:VA;0)	= 2000

TABLE I. Continued

HCP_A3 2 SUBLATTICES, SITES 1: .5 CONSTITUENTS: AG,BI,SN : VA
L(HCP_A3,AG,BI,VA;0) = +25077.78-12.05475*T L(HCP_A3,AG,BI,SN:VA;0) = 50000 L(HCP_A3,AG,SN:VA;0) = +1046.1+10.23693*T L(HCP_A3,AG,SN:VA;1) = -40505.5 L(HCP_A3,BI,SN:VA;0) = 2000
BCT_A5 1 SUBLATTICE CONSTITUENTS: AG,BI,SN
L(BCT_A5,AG,BI;0) = +25077.78-12.05475*T L(BCT_A5,AG,SN;0) = 18358.8 L(BCT_A5,BI,SN;0) = +3500-1.038*T L(BCT_A5,BI,SN;1) = -3710
RHOMBOHEDRAL_A7 EXCESS MODEL IS REDLICH-KISTER_MUGGIANU CONSTITUENTS: BI,SN
L(RHOMBOHEDRAL_A7,BI,SN;0) = +19720-22.6*T L(RHOMBOHEDRAL_A7,BI,SN;1) = -5760+11.834*T

Calculation of the thermodynamic properties of liquid Ag–Bi–Sn alloys

Katayama *et al.*⁷ recently measured the activity of tin using the fused salt EMF method at 900 K along the isoconcentration sections of Sn ($x_{Ag}/x_{Bi} = 1/3, 1/1$ and $3/1$). Based on these results, the concentration dependences of the excess Gibbs energy of mixing were obtained using the Darken Equation.¹⁵ These experimentally based results were used for comparison with the data from the present work, which were calculated using the optimized thermodynamic parameters for the constitutive binary systems. The excess Gibbs energies of mixing at 900 K for the ternary Ag–Bi–Sn system were calculated on the basis of the Redlich–Kister–Muggianu Model⁹ from the binary data only and using ternary parameters from the literature.⁵ Comparison between the Gibbs energy calculated from the binary prediction using ternary parameters and the experimental results⁸ is shown in Fig. 1.

It may be seen that experimental data could be thermodynamically very well described using ternary interaction parameters in the calculation procedure. Binary prediction alone did not give satisfactory results. The same trend of good agreement between the results calculated in this work and experimental data⁷ is shown in Fig. 2, in which the activities in three investigated isoconcentration sections from the tin corner with $x_{Ag}/x_{Bi} = 1/3, 1/1$ and $3/1$ at 900 K are presented.

Fair agreement between the experimental and the calculated values is observed for all the studied compositions. The calculated isoactivity curves at 900 K for every component are shown in Fig. 3.

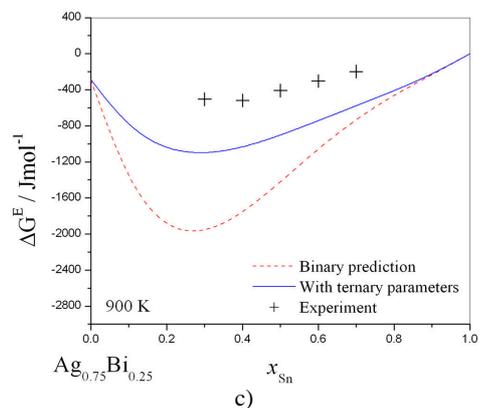
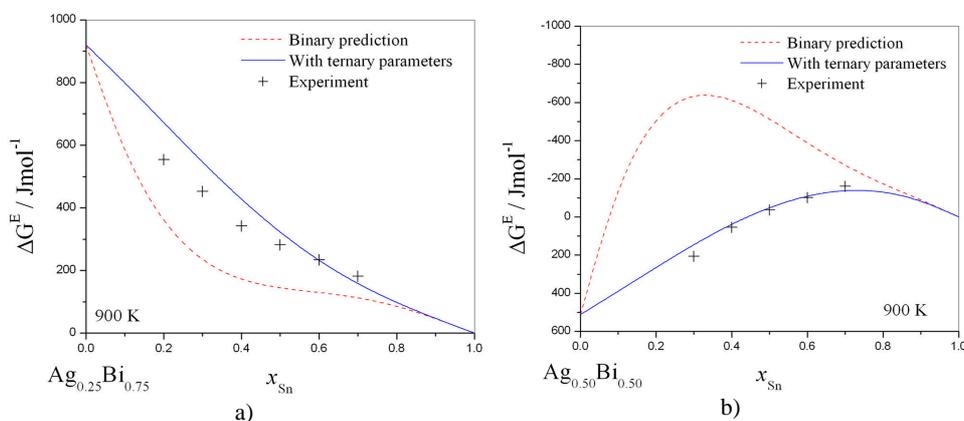


Fig. 1. Calculated and experimental integral molar Gibbs excess energy⁷ concentration dependences based on Calphad calculations and derived from experimental measurements for isoconcentration section from tin corner at 900 K with: a) $x_{Ag}/x_{Bi} = 1/3$; b) $x_{Ag}/x_{Bi} = 1/1$; c) $x_{Ag}/x_{Bi} = 3/1$.

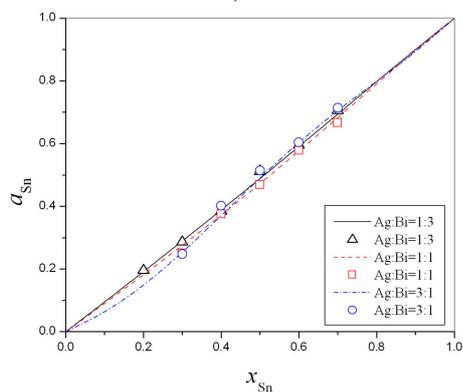


Fig. 2. Comparison of calculated tin activity (lines) and experimental values⁷ (symbols) in the Ag–Bi–Sn system at 900 K.

Furthermore, mixing enthalpies for some alloys in the Ag–Bi–Sn system were calculated and compared with mixing enthalpies of liquid alloys experimentally determined using direct reaction calorimetry.⁶ The results of the comparison between the enthalpies of formation calculated using ternary parameters and experimental values determined at 878 K (for two sections with molar ratio of $x_{Ag}/x_{Bi} = 1/3$ and $x_{Bi}/x_{Sn} = 1/3$), showing fair mutual agreement, are shown in Fig. 4.

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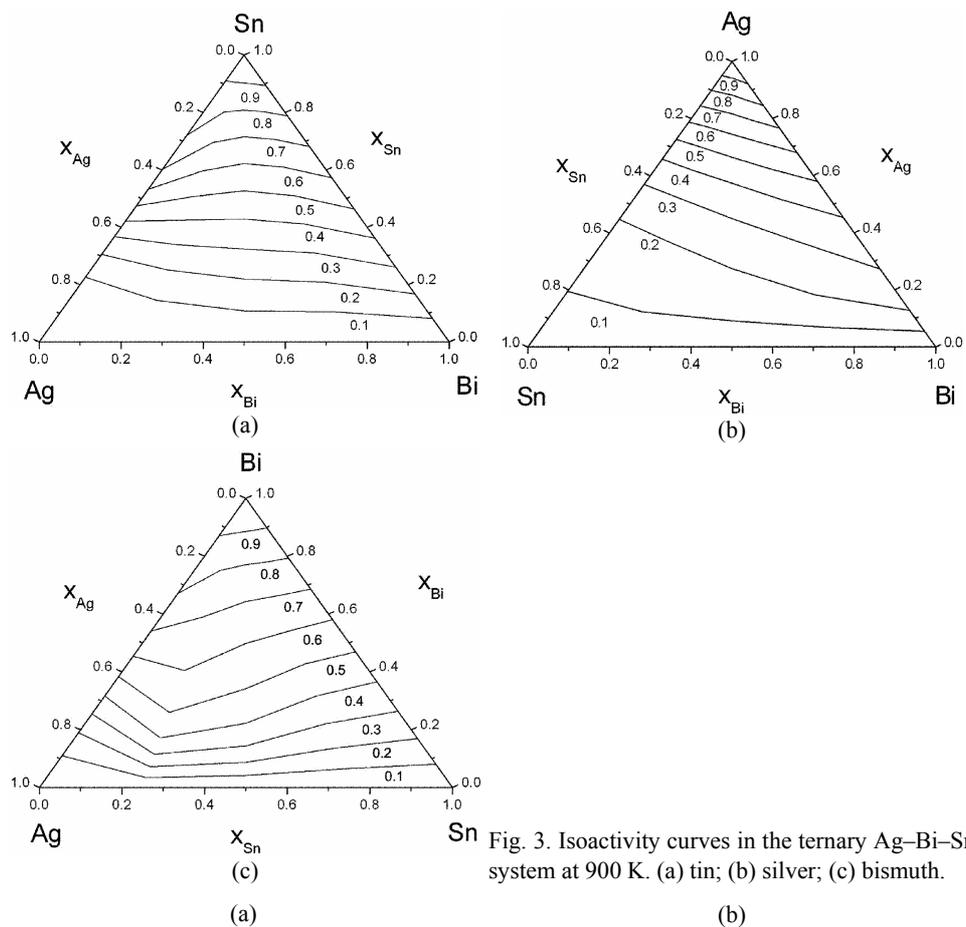


Fig. 3. Isoactivity curves in the ternary Ag–Bi–Sn system at 900 K. (a) tin; (b) silver; (c) bismuth.

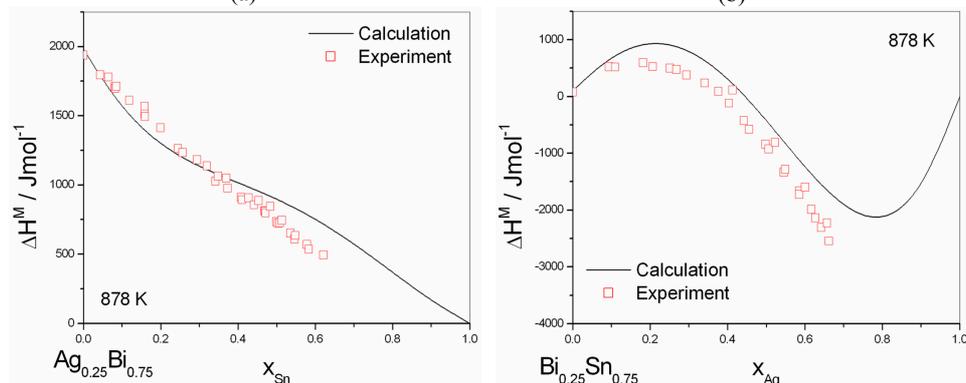


Fig. 4. Enthalpy of formation of Ag–Bi–Sn liquid alloys at the section of: a) $x_{Ag}/x_{Bi} = 1/3$; b) $x_{Bi}/x_{Sn} = 1/3$.

Investigation of the phase equilibria of the Ag–Bi–Sn ternary system

The phase diagrams for three vertical sections in this ternary system, Sn–AgBi, Ag–BiSn and Bi–AgSn, were calculated using optimized thermodynamic parameters⁵ from Table I. DTA measurements were used to check and confirm the calculated phase boundaries. The experimental results of thermal analysis, including the characteristic temperatures of the endothermic peaks, which occur during heating of the investigated samples in the three chosen sections, are presented in Table II.

TABLE II. The temperatures of liquidus and other phase transformations obtained by DTA for the samples in Ag–Bi–Sn system

Sample composition at. %	Temperature of the DTA peak / K	
	Liquidus	Other phase transformations
Ag:Bi=1:1		
Sn10Ag45Bi45	505	262
Sn20Ag40Bi40	495	136, 243, 411
Sn40Ag30Bi30	443	137, 167
Sn60Ag20Bi20	401	138, 172
Sn80Ag10Bi10	312	137, 194
Bi:Sn=1:1		
Sn45Ag10Bi45	381	139
Sn35Ag30Bi35	444	140, 180
Sn25Ag50Bi25	482	139, 183
Sn20Ag60Bi20	537	260, 373
Sn15Ag70Bi15	558	262
Sn5Ag90Bi5	814	–
Ag:Sn=1:1		
Sn45Ag45Bi10	481	138, 164
Sn35Ag35Bi30	485	138, 167
Sn25Ag25Bi50	476	139, 205
Sn15Ag15Bi70	428	139, 260
Sn5Ag5Bi90	271	141

The phase diagrams for three sections in the investigated system, Sn–AgBi, Ag–BiSn and Bi–AgSn, calculated using ThermoCalc software¹⁶ and including the obtained DTA results, are presented in Fig. 5.

As can be seen in Fig. 5, there is a good agreement between the calculated phase diagrams of the investigated sections and the experimental results obtained by DTA.

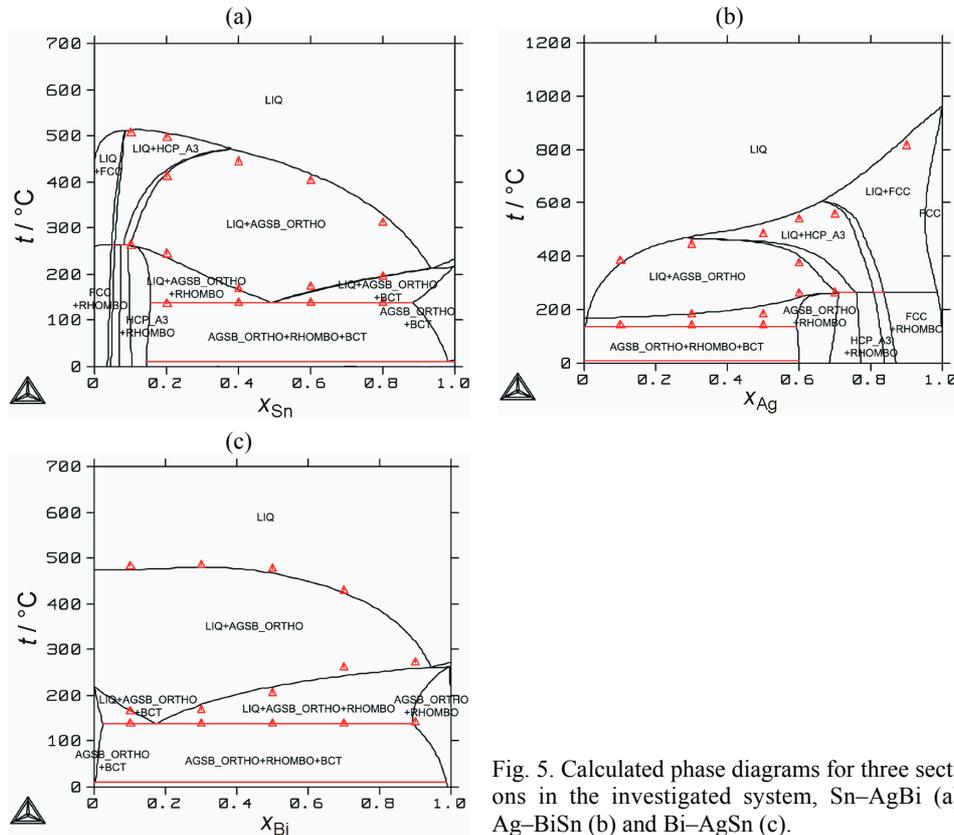


Fig. 5. Calculated phase diagrams for three sections in the investigated system, Sn–AgBi (a), Ag–BiSn (b) and Bi–AgSn (c).

CONCLUSIONS

The results of the calculation of thermodynamic properties and phase diagram in the Ag–Bi–Sn system are presented in this paper. The Gibbs excess energy was calculated using the Redlich–Kister–Muggianu model from binary data only and by applying a ternary correction term, using starting data given in the literature.⁵ It was shown that the ternary term significantly improves the agreement between the calculated and experimental-based results. The calculated results were compared with available experimental data reported in the literature. The phase diagrams for the vertical sections Sn–AgBi, Ag–BiSn and Bi–AgSn were calculated using ThermoCalc software. The calculated phase diagrams were compared with experimental DTA data from the present study. Good mutual agreement was noticed.

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ИЗВОД

ПРОРАЧУН ТЕРМОДИНАМИЧКИХ ВЕЛИЧИНА И ФАЗНИХ ДИЈАГРАМА
У НЕКИМ ПРЕСЕЦИМА Ag–Bi–Sn СИСТЕМАДРАГАНА ЖИВКОВИЋ¹, IWAO KATAYAMA², ДРАГАН МАНАСИЈЕВИЋ¹,
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У раду је извршен прорачун термодинамичких величина и фазних дијаграма у неким пресецима Ag–Bi–Sn система. Термодинамичке функције су прорачунате применом RKM модела и упоређене са експерименталним резултатима из литературе. Дијаграми изо-активних линија су конструисани за све три компоненте на 900 К. Прорачунати фазни дијаграми вертикалних пресека Sn–AgBi, Ag–BiSn и Bi–AgSn применом ThermoCalc програма су упоређени и потврђени резултатима ДТА мерења из овог рада.

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