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Prediction of phase equilibria in the In-Sb-Pb system

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Abstract: Binary thermodynamic data, successfully used for phase diagram calculations of the binary systems In–Sb, Pb–Sb and In–Pb, were used for the prediction of the phase equilibria in the ternary In–Sb–Pb system. The predicted equilibrium phase diagram of the vertical Pb–InSb section was compared with the results of differential thermal analysis (DTA) and optical microscopy. The calculated phase diagram of the isothermal section at 300 °C was compared with the experimentally (SEM, EDX) determined composition of phases in the chosen alloys after annealing. Very good agreement between the binary-based thermodynamic prediction and the experimental data was found in all cases. The calculated liquidus projection of the ternary In–Sb–Pb system is also presented.

Keywords: In-Sb-Pb system; phase diagram; thermodynamics.

INTRODUCTION

Knowledge of phase equilibria in ternary systems of the corresponding metals with elements of III–V compound semiconductors is an important step towards a better understanding of contact formation and presents a basis for the development of new and improved contact materials.

In previous studies related to phase equilibria in ternary systems with III–V compounds, the phase equilibria in Ga–Sb–Pb and In–Sb–Bi ternary systems were investigated,^{1,2} using experimental techniques (SEM–EDX and DTA) and the analytical CALPHAD approach. However, thermodynamic modeling of the ternary In–Sb–Pb system still has not been presented in the literature.

The aim of this study was to calculate phase equilibria of the In–Sb–Pb system according to the CALPHAD method^{3–5} and to compare the obtained results with experimentally based results from this work and the literature.

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THERMODYNAMIC MODELING

Pure elements

The pure solid elements at 298.15 K and 1.0 bar in their stable form were chosen as the reference state for the systems (SER). Version 4.4 of the SGTE unary database (scientific group thermodata Europe) of the phase stabilities for stable and metastable states of the pure elements was used.⁶

Binary systems

The thermodynamic descriptions of the binary alloys, *i.e.*, the In–Sb system,⁷ the Pb–Sb system⁸ and the In–Pb system,⁹ were taken from the literature.

Liquid and solid solution phases

The molar Gibbs energies of liquid and solid solution phases, referred to the enthalpies of the pure elements in their stable state at 298.15 K, ${}^{0}H_{i}^{\text{SER}}$ (298.15 K), are described by the sub-regular solution model with the Redlich–Kister polynomial as follows:

$$G_m^{\varphi} - \sum_{i=A,B,C} x_i^{\varphi 0} H_i^{\text{SER}} =$$

$$= \sum_{i=A,B,C} x_i^{\varphi} \left({}^0 G_i^{\varphi} - {}^0 H_i^{\text{SER}} \right) + RT \sum_{i=A,B,C} x_i^{\varphi} \ln \left(x_i^{\varphi} \right) + G^{\varphi,\text{xs}}$$
(1)

where $G^{\varphi,xs}$ represents the excess Gibbs energy of a ternary solution expressed by the Redlich–Kister–Muggianu expression:

$$G^{\varphi, xs} = x_{A}^{\varphi} x_{B}^{\varphi} \sum_{\nu=1}^{n} {}^{\nu} L_{A,B}^{\varphi} \left(x_{A}^{\varphi} - x_{B}^{\varphi} \right)^{\nu} + x_{B}^{\varphi} x_{C}^{\varphi} \sum_{\nu=1}^{n} {}^{\nu} L_{B,C}^{\varphi} \left(x_{B}^{\varphi} - x_{C}^{\varphi} \right)^{\nu} + x_{C}^{\varphi} x_{A}^{\varphi} \sum_{\nu=1}^{n} {}^{\nu} L_{C,A}^{\varphi} \left(x_{C}^{\varphi} - x_{A}^{\varphi} \right)^{\nu} + x_{A}^{\varphi} x_{B}^{\varphi} x_{C}^{\varphi} L_{A,B,C}^{\varphi}$$
(2)

where ${}^{\nu}L_{A,B}^{\varphi}$ is the temperature-dependent binary parameter optimized on the basis of the available thermodynamic and phase diagram data, and *i*, *j* are the elements of the system.

The term ${}^{\nu}L_{A,B,C}^{\varphi}$ is a ternary interaction parameter, which is expressed as:

$$x_{A}^{\varphi}x_{B}^{\varphi}x_{C}^{\varphi}L_{A,B,C}^{\varphi} = x_{A}^{\varphi}x_{B}^{\varphi}x_{C}^{\varphi}(x_{A}^{\varphi}{}^{0}L_{A,B,C}^{\varphi} + x_{B}^{\varphi,1}L_{A,B,C}^{\varphi} + x_{C}^{\varphi,2}L_{A,B,C}^{\varphi})$$
(3)

The terms $L_{i,j}^{\varphi}$, which can be temperature-dependent, are expressed by:

$${}^{\prime}L^{\varphi}_{i,j} = {}^{\nu}A^{\varphi}_{i,j} + {}^{\nu}B^{\varphi}_{i,j}T + \dots$$
(4)

InSb stoichiometric compound

The InSb phase is a stoichiometric compound. The Gibbs energy of the compound, *i.e.*, X_mY_n , is generally described as:

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PHASE EQUILIBRIA IN In-Sb-Pb SYSTEM

$$G_m^{X_m Y_n} = \frac{m}{m+n} G_X + \frac{n}{m+n} G_Y + \Delta G_{X_m Y_n}^{f}$$
(5)

where $\Delta G_{X_m Y_n}^{f}$ represents the Gibbs energy of formation per mole of atoms of the $X_m Y_n$ compound and is expressed by the following equation:

$$\Delta G_{X_m Y_n}^{\dagger} = A + BT \tag{6}$$

The Pb-In-Sb ternary system

There are only three references concerning the thermodynamic properties and phase equilibria of alloys of the Pb–In–Sb ternary system.

Predel and Gerdes¹⁰ determined the enthalpy changes of mixing molten InSb with liquid lead at 883 K using a high temperature calorimeter. The results were discussed with the aid of the regular solution model and also under the assumption of the existence of InSb associates in the ternary melt.

Geis and Peretti¹¹ experimentally investigated lead-rich and antimony-rich regions of the Pb–In–Sb ternary system and gave a partial liquidus projection for the concentration range InSb–Pb–Sb. Minić *et al.*¹² researched the thermodynamic properties of some alloys in the Pb–In–Sb ternary system using an Oelsen calorimetry and general solution model calculations.

EXPERIMENTAL

Alloys of the In–Sb–Pb system were prepared from the pure metals (99.99 %) by melting weighed amounts of indium, antimony and lead under an argon atmosphere.

After melting, alloys were subjected to a homogenizing annealing in evacuated glass capsules. The samples were annealed at 300 °C for 100 h. After annealing, the samples to be used for DTA measurements were cooled inside the furnace to the room temperature, while the samples for SEM–EDX investigation were quenched into ice water from 300 °C.

DTA Measurements were performed with a Derivatograph 1500 (MOM Budapest) apparatus under the following conditions: air atmosphere, heating rate 10 °C min⁻¹. The total mass of each sample was approximately 2 g. The precision of the measurement in the investigated temperature interval was ± 2 °C.

The equilibrium compositions in the quenched samples were determined using a JEOL scanning electron microscope with an accelerating voltage of 20 kV and an EDX analyzer.

Optical microscopy was performed using a Reichert MeF2 microscope.

RESULTS AND DISCUSSION

The values of the integral molar Gibbs excess energies, $G_{ij}^{\rm E}$, for the constitutive binary systems In–Sb, Pb–Sb and In–Pb, taken from Ansara *et al.*⁷, Ohtani and Ishida⁸ and Bolcavage *et al.*,⁹ respectively, were used as the starting binary thermodynamic data for the calculation. All these data, given in Table I, are included in the COST 531 binary database.¹³

Gibbs energy of the intermediate InSb phase was optimized by Ansara *et al.*⁷ as: G(ZINCBLENDE_B3,IN:SB;0)= 0.5*GHSERIN+0.5*GHSERSB -15849.3 + +.293139*T + 1.293581*T*LN(T) (298.14< T < 3000.00)

Calculation of the characteristic phase diagrams of the In–Sb–Pb system was performed using Thermo-Calc software (TC4A version).

Phase	Parameter	In-Pb ⁹	In-Sb ⁷	Pb-Sb ⁸
FCC_A1	$^{0}L_{A,B}$	4846.2-2.56363*T	-20000+15*T	11400-22.66*T
	$L_{A,B}$	305.1	-	-
LIQUID	$^{0}L_{A,B}$	3771.4-0.96292*T	25631.2+102.9324*T-	110 25*T
			-13.45816*T*LN(T)	110-2.5*1
	$^{1}L_{A,B}$	207.7	-2115.4-1.31907*T	-420+1.05*T
	$^{2}L_{A,B}$	-	2908.9	0.36*T
TETRAGONAL_A6	$^{0}L_{A,B}$	-3118.2	-	-
	$^{1}L_{A,B}$	3741.1	-	-
TET_ALPHA1	$^{0}L_{A,B}$	3207.99-2.1104311*T	-	-
	$^{1}L_{A,B}$	-2075.44+7.9804712*T	-	-
RHOMBOHEDRAL_A7	$^{0}L_{A,B}$	6000	15*T	21360-5.66*T

TABLE I. The Redlich-Kister parameters for the constitutive binary systems

In order to experimentally verify the calculated phase diagram of the InSb–Pb section, alloys with 20, 40, 60, 80 and 90 at. % of lead were studied in this work by means of DTA and optical microscopy.

The results of the DTA measurements are given in Table II, together with the interpretation of the various thermal effects. To test the reproducibility of the results, every measurement was repeated one more time. No significant temperature deviation was found between the first series and the repeated series of DTA measurements.

Composition at % Ph	t / °C		
Composition, at. 76 FU	Eutectic reaction	Liquidus (heating)	
20	297	480	
40	297	442	
60	297	399	
80	297	347	
90	298	_	

TABLE II. DTA Results for the quasi-binary InSb-Pb alloys

The phase diagram calculated from the DTA results obtained in this study is shown in Fig. 1.

The differential thermal analysis curves well confirmed the predicted lines of the investigated polythermal InSb–Pb section.

The predicted and experimentally determined eutectic temperatures are in excellent agreement (both at 297 °C) and with a very close eutectic concentration: 89 at.% Pb (calculated) and 90 at.% Pb (experimentally obtained). The liquidus temperatures obtained by DTA are little underestimated in comparison with the thermodynamic predicted ones.

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The results from this work are in accordance with the experimental results of Geis and Peretti¹¹ (299 °C and 89.2 at. % Pb).

A characteristic microphotograph recorded by optical microscopy for the samples with 40 at. % Pb is given in Fig. 2.





The results of SEM analysis are given in Table III and in Fig. 3a. The agreement between the predicted phases and the experimentally determined ones of samples 1 and 2 is perfect.

The calculated phase diagrams of the isothermal sections at 300 and 350 $^{\circ}$ C are shown in Fig. 3.

The predicted isothermal section of the In–Sb–Pb ternary system at 350 °C includes one three-phase region (InSb + rhombo + liquid), three two-phase regions (InSb + rhombo, InSb + liquid and rhombo + liquid) and one single-phase region (liquid). At 300 °C, the In–Sb–Pb phase diagram includes three three-phase regions (one InSb + rhombo + liquid region and two InSb + FCC + liquid regions), seven two-phase regions (two InSb + liquid regions, two liquid + FCC regions, one InSb + FCC region, one rhombo + liquid region and one InSb + rhombo region) and three single-phase regions (two liquid regions and one FCC region).

Theoretically Experimentally Exp. compositions Overall experimental Sample predicted determined of phases, at.% composition, at. % phases phases In Sb Pb 1 (61.1±1.2) In InSb InSb 50.6±0.4 49.4±0.3 (19.6±1.6) Sb 66.5±1.1 4.2±0.8 29.3±1.5 Liquid Liquid (19.3±1.2) Pb 2 (19.6±1.1) In Rhombo Rhombo 97.6±1.1 2.4±0.5 (61.2±1.5) Sb InSb InSb 50.5 ± 0.5 49.5±0.3 (19.2±0.9) Pb Liquid Liquid 1.4±0.3 25.3±0.4 73.3±1.3 a) b) In In 1 Ø 1.0 Ø. 0.9 0.8 0.8 0.7 ø. 0.6 +5 0.6 InSb+Lig Ø 0.5 e ø. InSb+Lig. 0.3 0.3 InSb+Liq. å 0.2 0.2 Rhombo InSb +Rhombo. ø. 0.1 Ø) 0 × 0.4 0.2 Ø 0.6 0.8 Ø 1 Ø Ø.2 0.4 0.6 0.8 1.0 PBLig.+FCC Pb X_{Pb} X_{Pb} Sb Sb Pb

TABLE III. Results of the SEM-EDX analysis



The liquidus projection of the investigated In–Sb–Pb ternary system was constructed based on the results of thermodynamic prediction. The obtained diagram is shown in Fig. 4.





CONCLUSION

The binary-based thermodynamic prediction of the characteristic phase diagrams in the In–Sb–Pb system was successfully performed using optimized thermodynamic parameters for the constitutive binary systems from the literature. The estimated phase diagram of the Pb–InSb vertical section shows very good agreement with the experimental results from this work and the literature data of Geis and Peretti.¹¹ The predicted phase diagram of isothermal section at 300 °C is in excellent agreement with the results of SEM–EDX analysis from this work. The calculated phase diagrams of isothermal sections at different temperatures were used for the construction of a liquidus projection of the investigated In–Sb–Pb ternary system. According to the results presented in this study, it could be concluded that the thermodynamic ternary parameters have a negligible influence on the equilibria of this ternary system.

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Извод

ПРЕДВИЂАЊЕ ФАЗНИХ РАВНОТЕЖА У In-Sb-Pb СИСТЕМУ

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Оптимизирани термодинамички подаци, успешно употребљени за прорачун равнотежних фазних дијаграма саставних бинарних система: In–Sb, Pb–Sb и In–Pb, су искоришћени за предвиђање равнотежних фазних дијаграма у In–Sb–Pb систему. Предвиђени фазни дијаграм вертикалног Pb–InSb пресека је упоређен са DTA резултатима и резултатима оптичке микроскопије. Прорачунати фазни дијаграм изотермалног пресека на 300 °C је упоређен са експериментално одређеним (SEM–EDX) саставима фаза у испитиваним узорцима после жарења. У свим случајевима је уочено веома добро међусобно слагање између резултата термодинамичког предвиђања и експерименталних резултата. Ликвидус пројекција In–Sb–Pb система је, такође, представљена.

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