

Phase diagram investigation and characterization of alloys in Bi-Ga₁₀Sb₉₀ section of Ga-Bi-Sb system

D. ŽIVKOVIĆ^{a*}, D. MINIĆ^b, D. MANASIJEVIĆ^a, N. TALIJAN^c, LJ. BALANOVIĆ^a,
A. MITOVSKI^a, V. ČOSOVIĆ^c, I. RANGELOV^a

^aUniversity of Belgrade, Technical Faculty, Bor (Serbia)

^bUniversity of Priština, Faculty of Technical Sciences, Kosovska Mitrovica (Serbia)

^cUniversity of Belgrade, Institute for Chemistry, Technology and Metallurgy, Belgrade (Serbia)

The results of phase equilibria investigation and characterization of the alloys in the Bi-Ga₁₀Sb₉₀ section of Ga-Bi-Sb system are presented in this paper. Phase diagram of the mentioned section has been calculated according to CALPHAD model, using Pandat software. In the frame of alloys characterization, structural, mechanical and electrical characteristics were determined using SEM-EDX analysis, microhardness and electroconductivity measurements.

(Received April 22, 2010; accepted June 16, 2010)

Keywords: Phase diagram, Characterization, Ternary alloys, Ga-Sb-Bi system

1. Introduction

Gallium-based alloys, especially multicomponent gallium antimonide- based alloys, have been a subject of different investigations for their wide application in electronics and other engineering practice. The knowledge of their phase diagram is important from theoretical and practical point of view, so main task in complete determination of such semiconducting materials is to investigate their thermodynamic properties and phase equilibria.

model, Hajra, Margules, Bale-Pelton) [4,5], but still not completely investigated, although some new results of phase equilibria of this system has been available in literature recently [6].

As a contribution to the completion of data concerning Bi-Ga-Sb system, the results including phase diagram, structural, mechanical and electrical characteristics investigation in the section from Bi corner with molar ratio of Ga:Sb = 1:9, given in Fig.1, are presented in this paper.

2. Experimental

The metals used for the preparation of selected samples were bismuth, gallium and antimony of 99.99% purity. Investigated compositions were with x_{Bi} equal to 0; 0.1;0.3;0.5;0.7 and 0.9.

For experimental investigation used in this work, SEM-EDX analysis, microhardness and electroconductivity measurements were applied.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX) analysis were performed on the electronic microscope Philips XL-300. The solution of (8M H₂SO₄ + 2g K₂Cr₂O₇) was used as etching agents for structure development.

Microhardness measurements were done using standard Vickers method, using 100g load in five points, taking average value.

Electrical conductivity of investigated materials was measured using three series of measurements on the standard apparatus SIGMATEST 2.069 (Foerster) - eddy current instrument for measurements of electrical conductivity of non-ferromagnetic metals, based on complex impedance of the measuring probe with diameter of 8mm.

All experiments were performed in an air atmosphere.

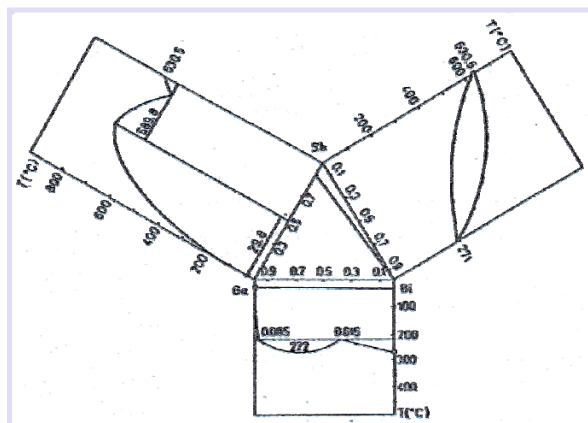


Fig. 1. Ternary system Bi-Ga-Sb with signed – investigated section Bi-Ga₁₀Sb₉₀ [3]

One of the interesting systems, among mentioned group of alloys, is the Bi-Ga-Sb system. This system has been thermodynamically analyzed in some sections, experimentally – using emf measurements [1] and Oelsen calorimetry [2,3], and analytically – using calculation procedures of thermodynamic predicting (general solution

3. Theoretical fundamentals

The basics of CALPHAD method [7,8], used in this paper for the calculation of phase equilibria, is a constrained minimization of Gibbs energy for a given temperature, pressure and overall composition, which is compatible with all currently available software packages for the modelling of thermodynamic properties and phase diagrams of multicomponent systems.

The molar Gibbs energy of a phase ϕ can be considered as the sum of a number of different contributions:

$$G_m^\phi = G_{ref}^\phi + G_{id}^\phi + G_E^\phi + G_{mag}^\phi + G_P^\phi + \dots \quad (1)$$

where G_{ref}^ϕ is the molar Gibbs energy of the weighted sum of the system constituents i (elements, species, compounds etc.) of the phase ϕ relative to the chosen reference state (typically the Stable Element Reference state - SER),

$$G_{ref}^\phi = \sum_{i=1}^n x_i \cdot G_i^\phi \quad (2)$$

and its temperature dependence is given by

$$G(T) = a + bT + cT \ln(T) + \sum_i d_i T^n \quad (3)$$

where a - d_i are adjustable coefficients.

In the case where the constituent in question is a stoichiometric compound, its contribution to the G_{ref}^ϕ is usually expressed by the Gibbs energy of formation relative to the chosen reference state, G_f ,

$$G_{ref}^\phi = \sum_{i=1}^n x_i \cdot G_i^\phi + G_f \quad (4)$$

but, there is also a contribution to the Gibbs energy from ideal random mixing of the constituents on the crystal lattice, denoted G_{id}^ϕ ,

$$G_{id}^\phi = RT \sum_{i=1}^n x_i \cdot \ln(x_i) \quad , i=1, \dots, n \quad (5)$$

for an n -constituent system.

G_E^ϕ is the excess Gibbs energy, which describes the influence of non-ideal mixing behaviour on the thermodynamic properties of a solution phase and is given by the Muggianu extension of the Redlich-Kister formalism [9,10]

$$G_E^\phi = \sum_{\substack{i,j=1 \\ i \neq j}}^n x_i x_j \sum_{z=0}^m L(x_i - x_j)^z + \sum_{\substack{i,j,k=1 \\ i \neq j \neq k}}^n x_i x_j x_k L_{ijk} \quad z=0, \dots, m \quad (6)$$

where the interaction parameters, describing the mutual interaction among constituents i and j , are denoted as zL . The liquid phase and solid solution phases are modeled in this way, but more complex phases, such as intermetallic compounds, are usually modeled using the compound energy formalism [11].

4. Results and discussion

In the first part of this paper, phase diagram calculation according to CALPHAD method [7,8], was done. Therefore, the phase stability equations compiled by Dinsdale [12] were used for the thermodynamic functions of the pure elements in their stable and metastable states, while starting binary thermodynamic data for the Bi-Ga, Bi-Sb and Ga-Sb subsystems were taken from Refs.[13-15], respectively. The phases from mentioned binaries, considered for thermodynamic binary-based prediction with their crystallographic data, are listed in Table 1, while optimized unary and binary thermodynamic data used in this work are given in Appendix.

Table 1. The phases considered for thermodynamic binary based prediction –their crystallographic data and database names

Phase-common name	Prototype	Pearson Symbol	Space Group	Thermodynamic database name
liquid				LIQUID
(Bi)(Sb)	α As	$hR2$	$R3m$	RHOMBO_A7
(Ga)	α Ga	$oC8$	$Cmca$	ORTHORHO MBIC (ORT)
GaSb	ZnS	$cF 8$	$F43m$	ZINCBLLENDE B3

Based on data presented in Table 1 and Appendix, following the CALPHAD procedure described in theoretical fundamentals and using Pandat Software, phase diagram of the investigated section Bi-Ga₁₀Sb₉₀ was obtained and shown in Fig. 2. Comparison with our previous DTA results on this system [3] was done and shown in the same figure, showing good agreement between experimental and calculated phase diagram.

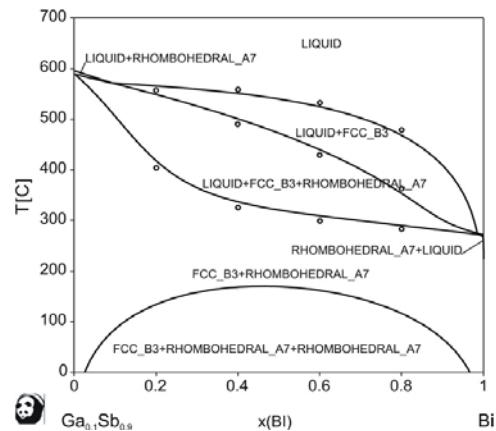


Fig. 2. Calculated phase diagram of the Bi-Ga₁₀Sb₉₀ section (lines - this work) compared with DTA results (circles - Ref. [3]).

In the second part of this work, characterization of the selected alloys in the Bi-Ga₁₀Sb₉₀ section in the Bi-Ga-Sb system was done.

SEM-EDX analysis was used for structural analysis and determination of chemical composition of coexisting phases presented in the investigated section. The results

obtained by SEM-EDX analysis, including SEM microphotographs and experimental determination of compositions, are given in Fig.3 and Table 3, respectively.

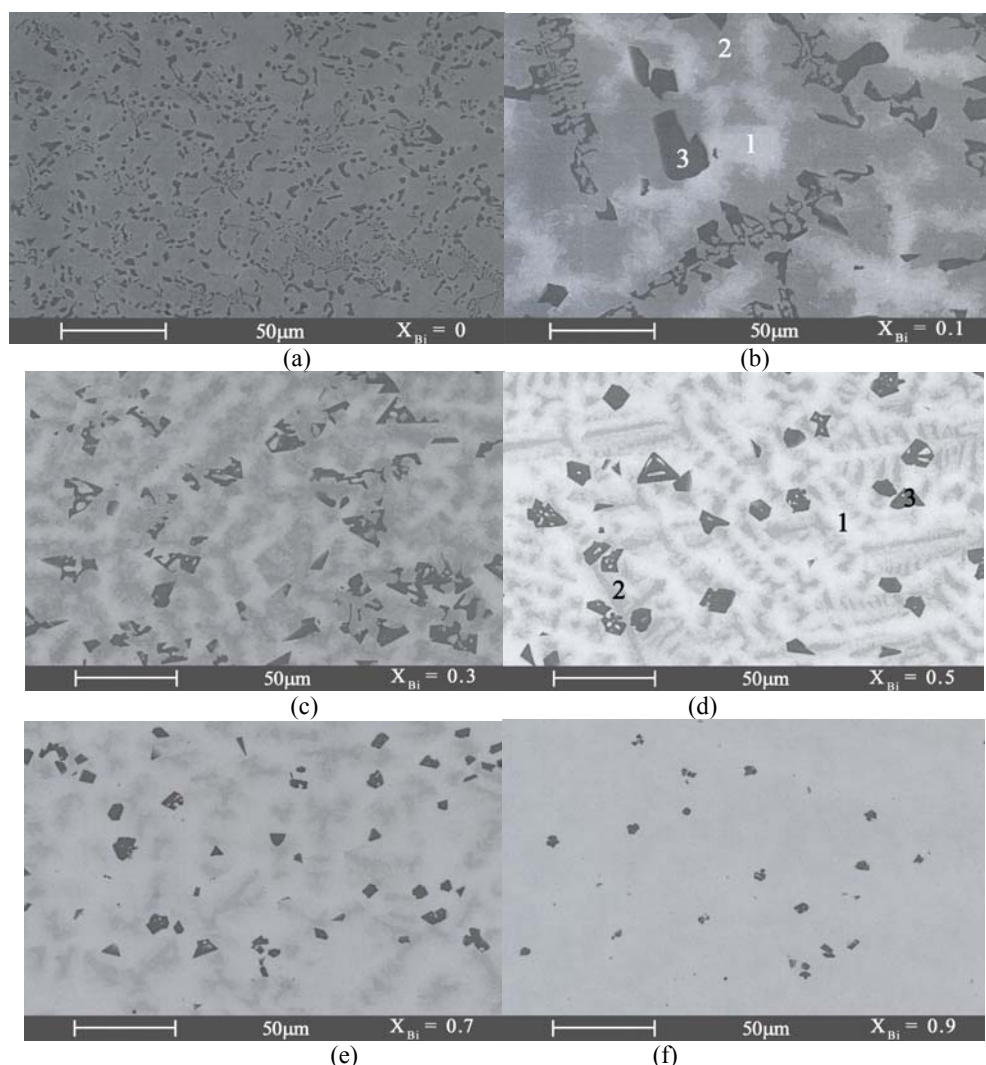


Fig. 3. SEM microphotographs for the alloys with x_{Bi} equal to 0 (a); 0.1 (b); 0.3 (c); 0.5 (d); 0.7 (e); 0.9 (f) (1 – light gray phase RHOMBO-A7 (Bi); 2 – dark gray phase RHOMBO_A7 (Sb); 3 – black phase ZINCBLLENDE_B3 (GaSb))

Tab. 3. EDX results for: (a) experimental determination of compositions and (b) experimental composition of phases

Alloy composition	Experimentally determined overall composition		
	Bi	Ga	Sb
Ga ₁₀ Sb ₉₀	-	11.32	88.68
Bi ₁₀ Ga ₉ Sb ₈₁	10.30	8.90	80.80
Bi ₃₀ Ga ₇ Sb ₆₃	31.42	6.4	62.18
Bi ₅₀ Ga ₅ Sb ₄₅	49.93	4.23	45.84
Bi ₇₀ Ga ₃ Sb ₂₇	70.32	3.55	26.14
Bi ₉₀ Ga ₁ Sb ₉	89.96	0.95	9.09

b

Experimentally determined overall composition	Experimentally determined phases	Experimentally determined compositions of phases [at.%]		
		Bi	Ga	Sb
10.30 at.%Bi 8.90 at.% Ga 80.80 at.%Sb	RHOMBO_A7 (Bi) RHOMBO_A7 (Sb) ZINCBLLENDE_B3 (GaSb)	77.3 4.78	2.07 - 48.56	20.63 95.22 51.44
49.93 at.%Bi 4.23 at.% Ga 45.84 at.%Sb	RHOMBO_A7 (Bi) RHOMBO_A7 (Sb) ZINCBLLENDE_B3 (GaSb)	77.3 25.55	4.51 0.4 49.5	18.17 74.05 50.5

Obtained SEM-EDX results confirmed experimentally overall alloys compositions and indicated to following phases present in the system (Fig. 3): black phase responds to GaSb (ZINCBLLENDE_B3); while dark and light gray phases are related to Bi-Sb solid solution (RHOMBO_A7) rich on Sb and on Bi, respectively.

The results of microhardness measurements are shown in Fig. 4, in the form of microhardness dependence on antimony composition. The microhardness values were measured for the light gray phase (RHOMBO_A7 – Bi-Sb solid solution rich on Bi) and was found to lie between 25 and 59 HV corresponding to the applied load of 100 g. It may be noticed that microhardness values increases uniformly with bismuth content increase, following the relation: $HV = -45.085x_{Bi}^2 + 71.183x_{Bi} + 29.845$.

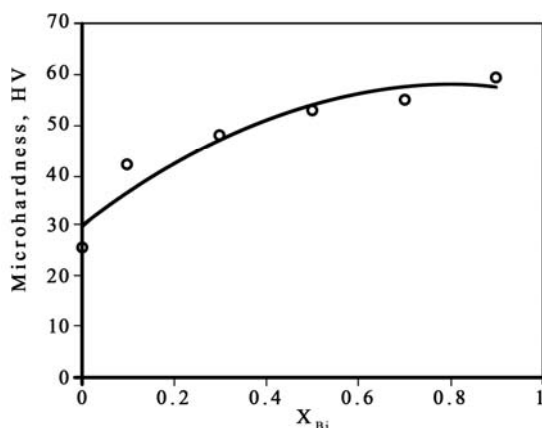


Fig. 4. Microhardness vs. composition for chosen alloys in the Bi-Ga₁₀Sb₉₀ section

The results of electrical conductivity measurements are presented in Table 4. As can be seen, the electrical conductivity was given for only two samples, because the other investigated samples didn't show any response during measurement.

Table 4. Measured values of electrical conductivity for investigated Au-In-Sb alloys.

x_{Bi}	Electroconductivity (MS/m)
0.5	0.4245
0.7	1.1883

5. Conclusions

The Bi-Ga-Sb alloys from the section with molar ratio Ga:Sb = 1:9 has been investigated in order to determine the phase diagram and characterize selected samples. Phase diagram of the Bi-Ga₁₀Sb₉₀ section was calculated using CALPHAD approach and Pandat Software based on available optimized unary and binary thermodynamic parameters. Obtained diagram showed good agreement in

comparison with experimental DTA results taken from literature. Structural and phase analysis has been done using SEM-EDX analysis, confirming experimentally overall alloys compositions and existence of three phases presented - black phase responding to GaSb (ZINCBLLENDE_B3); as well as dark and light gray phases related to Bi-Sb solid solution (RHOMBO_A7) rich on Sb and on Bi, respectively. More, the values of microhardness and electroconductivity have been measured and presented in the paper.

Acknowledgement

This work was supported by Ministry of Science and Technology Development, Republic of Serbia (Project No. 142043). Calculations were performed using PANDAT software.

References

- [1] I. Katayama, J. I. Nakayama, T. Ikura, Z. Kozuka and T. Iida, Mater. Trans. JIM, **34**, 792 (1993).
- [2] D. Živković, Ž. Živković, J. Šesták, CALPHAD, **23**, 113 (1999).
- [3] D. Živković, Ž. Živković, B. Vučinić, J. Therm. Anal. Calor., **61**, 263 (2000).
- [4] D. Živković, Ž. Živković, L. Stuparević, S. Rančić, J. Therm. Anal. Calor., **65**, 805 (2001).
- [5] D. Živković, Ž. Živković, Metalurgija (Journal of Metallurgy), **5**(3), 209 (1999). (In Serbian)
- [6] D. Minić, D. Manasijević, D. Živković, J. Stajić-Trošić, J. Djokić, D. Petković, Materials Science and Technology, DOI 10.1179/174328409X430537 (2009, in print)
- [7] N. Saunders, A. P. Miodownik, CALPHAD (A Comprehensive Guide), Elsevier, London, 1998.
- [8] H. L. Lukas, S. G. Fries, B. Sundman, Computational Thermodynamics, Cambridge University Press, Cambridge, UK 2007.
- [9] O. Redlich, A. Kister, Indust. Eng. Chem. **40**, 345 (1948).
- [10] Y.M. Muggianu, M. Gambino, J.-P. Bros, J. Chim. Phys. **72**, 83 (1975).
- [11] J.O. Andersson, A. Fernandez-Guillermet, M. Hillert, B. Jansson, B. Sundman, Acta Metall. **34**, 437 (1986).
- [12] A. T. Dinsdale, "SGTE unary database, version. 4.4" (www.sgte.org)
- [13] C. Girard: Thesis, University of Provence, Marseille 1985.
- [14] J. Vizdal, M. H. Braga, A. Kroupa, K. W. Richter, D. Soares, L. F. Malheiros, J. Ferreira, CALPHAD **31**(4), 438 (2007).
- [15] I. Ansara, C. Chatillon, H.L. Lukas, T. Nishizawa, H. Ohtani, K. Ishida, M. Hillert, B. Sundman, B.B. Argent, A. Watson, T.G. Chart, T. Anderson, Calphad **18**, 177 (1994).

Appendix*Optimised unary and binary thermodynamic data for Bi-Ga-Sb system used in present study*

LIQUID	
CONSTITUENTS: BI,GA,SB	
G(LIQUID,BI;0)-H298(RHOMBO A7,BI;0) =	
+3428.29+107.782416T-28.4096529Tln(T)+0.012338888T ² -8.381598E-06T ³ -5.9549E-19T ⁷ (298.14<T< 544.54)	[12]
+41544.282-414.460769T+51.8556592Tln(T)-0.075311163T ² +1.3499885E-05T ³ -3616168T ⁻¹ (544.54<T< 800.00)	[12]
+290.595+161.738553T-35.9824Tln(T) +0.0074266T ² -1.046E-06T ³ (800.00<T< 1200.00)	[12]
+3754.947+103.961021T-27.196Tln(T) (1200.00<T< 3000.00)	[12]
G(LIQUID,GA;0)-H298(ORT,GA;0) =	
+5491.298-18.073995T-7.017E-17T ⁷ +GHSERGA (200.00<T< 302.92)	[12]
+5666.455-18.681147T-1.645E+23T ⁻⁹ +GHSERGA (302.92<T< 4000.00)	[12]
G(LIQUID,SB;0)-H298(RHOMBO A7,SB;0) =	
+10579.47+134.231525T-30.5130752Tln(T)+0.007748768T ² -3.003415E-06T ³ +100625T ⁻¹ -1.74847E-20T ⁷ (298.14<T< 903.78)	[12]
+8175.359+147.455986T-31.38Tln(T) (903.78<T< 2000.00)	[12]
L(LIQUID,BI,GA;0) = +8401.6+.996135T	[13]
L(LIQUID,BI,GA;1) = -560.9-2.43423T	[13]
L(LIQUID,BI,GA;2) = +754.8-0.682275T	[13]
L(LIQUID,BI,GA;3) = -1162.5	[13]
L(LIQUID,BI,SB;0) = +2230+0.06T	[14]
L(LIQUID,GA,SB;0) = -13953.8+71.0787T-9.6232Tln(T)	[15]
L(LIQUID,GA,SB;1) = +1722.9-1.92588T	[15]
L(LIQUID,GA,SB;2) = 2128.3	[15]
RHOMBO_A7	
CONSTITUENTS: BI,SB	
G(RHOMBO A7,BI;0)-H298(RHOMBO A7,BI;0) = +GHSERBI=	
-7817.776+128.418925T-28.4096529Tln(T)+12.338888E-3T ² -8.381598E-6T ³ (298.14<T< 544.55)	[12]
30208.022-393.650351T+51.8556592Tln(T)-75.311163E-3T ² +13.499885E-6T ³ -3616168T ⁻¹ +166.145E23T ⁻⁹ (544.55<T< 800.00)	[12]
-11045.664+182.548971T-35.9824Tln(T)+7.4266E-3T ² -1.046E-6T ³ +166.145E23T ⁻⁹ (800.00<T< 1200.00)	[12]
-7581.312+124.77144T-27.196Tln(T)+166.145E23T ⁻⁹ (1200.00<T< 3000.00)	[12]
G(RHOMBO A7,SB;0)-H298(RHOMBO A7,SB;0) = +GHSERSB=	
-9242.858 + 156.154689T - 30.5130752Tln(T) + 7.748768E-3 T ² - 3.003415E-6 T ³ + 100625T ⁻¹ (298.15 < T < 903.78)	[12]
-11738.83 + 169.485872T -31.38Tln(T) +1616.849E24 T ⁻⁹ (903.78 < T < 2000.00)	[12]
L(RHOMBO A7,BI,SB;0) = +10150-6.3T	[14]
L(RHOMBO A7,BI,SB;1) = 150	[14]
ORT	
CONSTITUENTS: GA	
G(ORT,GA;VA;0)-H298(ORT,GA;0) = +GHSERGA=	
-21312.331 + 585.263691T - 108.2287832Tln(T) + 227.155636E-3T ² - 118.575257E-6 T ³ + 439954T ⁻¹ (200.00 < T < 302.91)	[12]
-7055.643 + 132.73019T - 26.0692906Tln(T) + 0.1506E-3T ² - 0.040173E-6T ³ - 118332T ⁻¹ + 164.547E21T ⁻⁹ (302.91 < T < 4000.00)	[12]

ZINCBLLENDE_B3	
CONSTITUENTS: GA : SB	
G(ZINCBLLENDE_B3,GA:SB;0)-0.5 H298(ORT,GA;0)-0.5 H298(RHOMBO_A7,SB;0)=	
-21738.1-10.53764T+2.692876TLN(T)-0.00137791T ² +0.5GHSEGA+0.5GHSERSB (200.00<T< 4000.00)	[15]

*Corresponding author: dzivkovic@tf.bor.ac.yu;
dzmaca@yahoo.com