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THERMODYNAMIC AND STRUCTURAL INVESTIGATION OF THE Ag-In-Sb SYSTEM

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The Ag-In-Sb ternary system presents one of the possible lead-free solder candidates. Therefore, the results of thermodynamic study of the alloys in the Ag-In-Sb alloys, obtained using general solution model, are presented in the paper. Obtained data for partial and integral molar thermodynamic quantities in the temperature interval 1000-1200K are given. The characterization of these alloys have been done using DTA, XRD, SEM and optic microscopy, which enabled the construction of the Ag-In-Sb phase diagram in the concentration range up to 60 wt. % Ag.

Key words: *thermodynamics, lead-free solder alloys, Ag-In-Sb system*

Termodinamska i strukturna ispitivanja Ag-In-Sb sustava. Ag-In-Sb ternarni sustav predstavlja potencijalni novi bezolovni materijal za lemljenje. U ovom radu su prikazani rezultati termodinamskog ispitivanja presijeka legura Ag-In-Sb dobiveni primjenom općeg modela rastvora. Rezultati obuhvaćaju parcijalne i integralne termodinamske veličine u temperaturnom području 1000-1200 K. Karakterizacija legura je izvedena primjenom DTA, XRD, SEM i optičke mikroskopije, što je omogućilo konstrukciju faznog dijagrama Ag-In-Sb sustava u koncentracijskom intervalu do 60 tež. % Ag.

Ključne riječi: *termodinamika, bezolovni materijali za lemljenje, Ag-In-Sb sustav*

INTRODUCTION

There are two primary driving forces that affect the requirements of lead-free solders for electronics and microelectronics applications: health concerns due to the toxicity and health hazard of lead and the heightened demands on the level of performance of solder joints due to the increased density and complexity of circuitry, driven by market demands [1].

Therefore, a great deal of effort has been put into the development of different lead-free solder alloys [2], due to a certain criteria which must be taken into account and met before a lead-free solder may be put into use, such as: physical reliability, temperature requirements, compatibility with parts/processes and repairs/rework. One among recently investigated solder-candidates is the Ag-In-Sb system, usually applied for electronic assembly [1,3] and presenting a constitutive part of an interesting multi-component material for optical recording [4].

The Ag-In-Sb system has been a subject of different studies [5 - 11], but not explored completely, although literature data on the constitutive binaries are numerous [12 - 35]. Among the references on ternary Ag-In-Sb alloys, there are some works on the phase equilibria investigations [5 - 7] and only two thermodynamic researches [8, 9]. Considering the study of phase equilibria, [5, 6] point out to the existence of ternary eutectic, based on the results of thermal and X-ray analysis of some Ag-In-Sb alloys. Recently, comparison of phase equilibria prediction to experimental data at 473K for the Ag-In-Sb system was presented by Buchtova et al. [7]. In the frame of thermodynamic analysis of the Ag-In-Sb system, Itabashi et al. [6] performed EMF measurements with zirconia solid electrolyte for determination of indium activities in some sections of the investigated system in temperature range from 970 to 1280 K, while Gather et al. [7] determined the enthalpies of mixing in a liquid state for the Ag-In-Sb system using a heat flow calorimeter.

Due to the momentary shortage in referent data, an unpretentious contribution to the better knowledge of the Ag-In-Sb system is given in this paper, through the investigations of thermodynamic and structural properties of the alloys in the Ag-In-Sb section.

EXPERIMENTAL

Experimental investigations presented in this paper were done using DTA, SEM and XRD analysis.

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DTA analysis was done on derivatograph MOM, Budapest (Hungary), at the heating rate of 10 K/min in an air atmosphere, while Al_2O_3 was used as a referent material during measurements.

XRD analysis was performed on Siemens apparatus, using Cu-anticathode and Ni-filters (40kV, 20mA).

SEM analysis was performed on JEOL-JSM T20 scanning microscope, while optic microscopy was done using Reichert MeF2 microscope. Solution (32g $FeCl_3$ + 100 ml H_2O_2 + 100 ml H_2O) and concentrated H_2O_2 were used as the etching agents for the samples prepared according to the standard metallographic procedure.

All experiments were carried out in an air atmosphere, with Ag, In and Sb metals of p.a. purity. Composition and masses of the experimentally investigated alloys are given in Table 1.

Table 1. **Composition and masses of the experimentally investigated samples**
Tablica 1. **Sastavi i mase eksperimentalno ispitivanih uzoraka**

Sample	Ag % wt	In % wt	Sb % wt	xAg	xIn	xSb	mAg g	mIn g	mSb g
A1	0	48,54	51,46	0,0	0,5	0,5	0,0	1,3538	1,4355
A2	10	43,68	46,32	0,109	0,446	0,446	0,2886	1,2608	1,3369
A3	20	38,83	41,17	0,215	0,392	0,392	0,5980	1,1611	1,2311
A4	30	33,97	36,03	0,319	0,340	0,340	0,9306	1,0539	1,1175
A5	40	29,12	30,88	0,422	0,289	0,289	1,2889	0,9384	0,9950
A6	50	24,27	25,73	0,523	0,238	0,238	1,6762	0,8135	0,86264
A7	60	19,41	20,59	0,622	0,189	0,189	2,0960	0,6782	0,7191

THEORETICAL FUNDAMENTALS

Beside main traditional methods representing the ternary thermodynamic properties based on three corresponding binary systems, a general solution model has been provided [36, 37].

The basic equations of this model are given as follows:

$$\begin{aligned}\Delta G^E = {} & x_1x_2\left[A_{12}^0 + A_{12}^1(x_1 - x_2) + A_{12}^2(x_1 - x_2)^2\right] \\ & + x_2x_3\left[A_{23}^0 + A_{23}^1(x_2 - x_3) + A_{23}^2(x_2 - x_3)^2\right] \\ & + x_3x_1\left[A_{31}^0 + A_{31}^1(x_3 - x_1) + A_{31}^2(x_3 - x_1)^2\right] + fx_1x_2x_3,\end{aligned} \quad (1)$$

where A_{ij}^0, A_{ij}^1, A_{ij}^2 are parameters for binary system "*ij*" independent of composition, only relying on temperature, which have been used in the regular type equation:

$$\begin{aligned}\Delta G_{ij}^E = {} & X_iX_j\left[A_{ij}^0 + A_{ij}^1(X_i - X_j)\right. \\ & \left. + A_{ij}^2(X_i - X_j)^2 + \ldots + A_{ij}^n(X_i - X_j)^n\right],\end{aligned} \quad (2)$$

where X_i and X_j indicate the mole fraction of component "*i*" and "*j*" in "*ij*" binary system. The function *f* is the ternary interaction coefficient expressed by

$$\begin{aligned}f = {} & (2\xi_{12} - 1)\left\{A_{12}^2\left[(2\xi_{12} - 1)x_3 + 2(x_1 - x_2)\right] + A_{12}^1\right\} \\ & (2\xi_{23} - 1)\left\{A_{23}^2\left[(2\xi_{23} - 1)x_1 + 2(x_2 - x_3)\right] + A_{23}^1\right\} \\ & (2\xi_{31} - 1)\left\{A_{31}^2\left[(2\xi_{31} - 1)x_2 + 2(x_3 - x_1)\right] + A_{31}^1\right\},\end{aligned} \quad (3)$$

where ξ_{ij} are the similarity coefficients defined by η_i called the deviation sum of squares:

$$\xi_{ij} = \frac{\eta_i}{\eta_i + \eta_j}, \quad (4)$$

where

$$\begin{aligned}\eta_{\mathrm{I}} &= \int_{X_i=0}^{X_i=1}\left(\Delta G_{12}^E - \Delta G_{13}^E\right)^2 \mathrm{d}X_1, \\ \eta_{\mathrm{II}} &= \int_{X_i=0}^{X_i=1}\left(\Delta G_{21}^E - \Delta G_{23}^E\right)^2 \mathrm{d}X_2, \\ \eta_{\mathrm{III}} &= \int_{X_i=0}^{X_i=1}\left(\Delta G_{31}^E - \Delta G_{32}^E\right)^2 \mathrm{d}X_3\end{aligned} \quad (5)$$

and

$$\begin{aligned}X_{1(12)} &= x_1 + x_3\xi_{12}, \\ X_{2(23)} &= x_2 + x_1\xi_{23}, \\ X_{3(31)} &= x_3 + x_2\xi_{31}.\end{aligned} \quad (6)$$

In all given equations, ΔG^E and ΔG_{ij}^E correspond to the integral molar excess Gibbs energies for ternary and binary systems, respectively, while x_1, x_2, x_3 correspond to the mole fraction of components in investigated ternary system.

RESULTS AND DISCUSSION

The first part of the investigations presented in this paper was the calculation of thermodynamic properties of the alloys in the Ag-In-Sb system. The alloys with molar content of silver equal to 0,1; 0,2; 0,3; 0,4; 0,5; 0,6; 0,7; 0,8 and 0,9 were used for the purpose of thermodynamic calculation.

Basic data for the calculation were the values of integral molar Gibbs excess energies, ΔG_{ij}^E, for the constitutive binary systems Ag-In, In-Sb and Sb-Ag taken from Moser

et al. [23], Cui et al. [26] and Oh et al. [34], respectively *(COST 531 binary database* [38]). Redlich-Kister parameters for the constituting binaries in the temperature range 1000-1200K, are given in Table 2.

Table 2. **Redlich-Kister parameters for the constitutive binaries**
Tablica 2. **Redlich-Kister parametri za sastavne binarne sustave**

System	L^0 / T	L^1 / T	L^2 / T	L^3 / T
Ag-In	– 14403,297 – 8,176T	– 15551,028 – 2,664T	– 710,629 – 5,293T	3955,27
In-Sb	– 25631,2 + 102,9324T – 13,45816Tln(T)	– 2115,41 – 1,31907T	2908,9835	0
Ag-Sb	– 821,8 – 9,6561T	– 19309 + 4,4239T	– 10381,2	0

Further, for the purpose of calculation according to the general solution model, related similarity coefficients were determined using Eq. (6) at the investigated temperatures and given in Table 3.

Table 3. **Determined similarity coefficients for Ag-In (1-2), In-Sb (2-3) and Sb-Ag (3-1) systems at 1000, 1100 and 1200 K**
Tablica 3. **Proračunati koeficijenti sličnosti za Ag-In (1-2), In-Sb (2-3) i Sb-Ag (3-1) sustave na 1000, 1100 i 1200 K**

T / K	ξ_{12}	ξ_{23}	ξ_{31}
1200	0,510693	0,776189	0,216467
1100	0,530379	0,747229	0,230489
1000	0,555518	0,707431	0,24863

The graphical presentation of the selected binary compositions for three constitutive binaries in the Ag-In-Sb system at the temperature of 1200K, shown in Figure 1.,

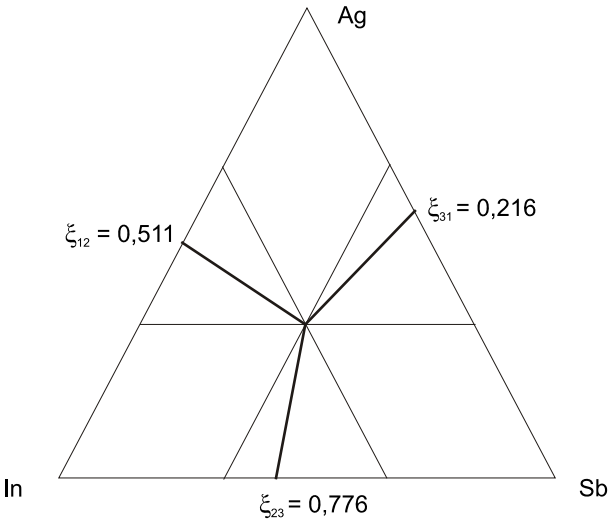

Figure 1. **The selected binary compositions for three binaries in the ternary system Ag-In-Sb according to general solution model at 1200K (shown as bold solid lines)**
Slika 1. **Odabrani binarni sastavi za tri binaran sustav u ternarnom Ag-InSb sustavu prema općem modelu rastvora na 1200 K (dani kao podebljane pune linije)**

confirms symmetric nature of the investigated lead-free solder candidate system, as was also stated in [7].

The values of integral molar Gibbs excess energies for the ternary alloys in Ag-In-Sb system, calculated using general solution model, are presented graphically in Figure 2. and given in the form of polynomial expressions:

$$\Delta G^E = 10052x_{\mathrm{Ag}}^3 - 1790,8x_{\mathrm{Ag}}^2 - 4329,7x_{\mathrm{Ag}} - 4003,9; \quad T = 1000\mathrm{K},$$

$$\Delta G^E = 11070x_{\mathrm{Ag}}^3 - 2568,9x_{\mathrm{Ag}}^2 - 4465,2x_{\mathrm{Ag}} - 4112,1; \quad T = 1100\mathrm{K},$$

$$\Delta G^E = 9745,3x_{\mathrm{Ag}}^3 - 509,17x_{\mathrm{Ag}}^2 - 5405x_{\mathrm{Ag}} - 4218,6; \quad T = 1200\mathrm{K}.$$

It can be noticed that integral molar excess Gibbs energies are negative at all investigated temperatures in the whole concentration range, with a minimum value of about –6 kJ/mol at the equiatomic composition. Also, derived

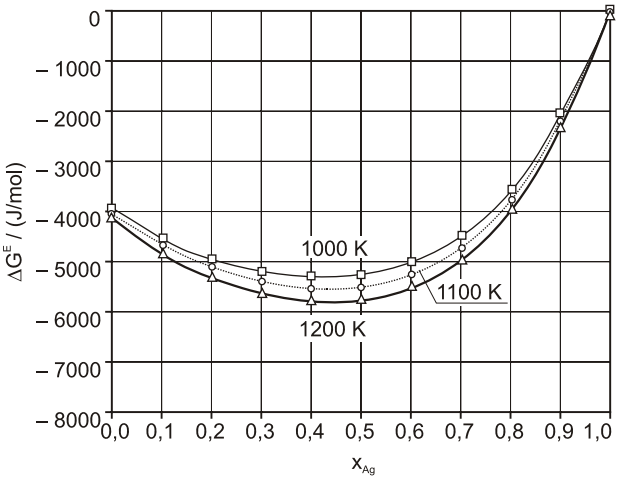

Figure 2. **Integral molar excess Gibbs energies of investigated alloys in Ag-In-Sb system at different temperatures**
Slika 2. **Integralne molarne ekscesne Gibbsove energije ispitivanih legura u ternarnom Ag-In-Sb sustavu na različitim temperaturama**

partial thermodynamic properties for silver point out to the negative deviation from ideal behavior, changing negligibly with temperature in the range 1000 - 1200 K, as can be seen from the Figure 3.

Comparison with literature data, which include the results from [10] and [11], calculated according to the Redlich-Kister-Muggianu method using ternary interaction parameters, is given in Figure 4. Reasonable agreement between these data may be noticed.

In the other part of the Ag-In-Sb system analysis, the samples were characterized using DTA, SEM and XRD methods.

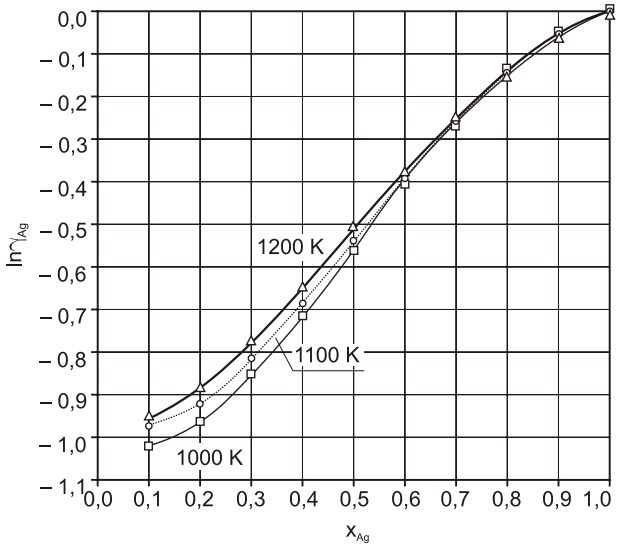

Figure 3. **Dependencies of $\ln\gamma_{Ag}$ vs. composition for investigated alloys in Ag-In-Sb system at different temperatures**

Slika 3. **Ovisnosti $\ln\gamma_{Ag}$ o sastavu ispitivanih legura u Ag-InSb sustavu na različitim temperaturama**

The temperatures of characteristic endothermic effects, obtained by DTA measurements for the concentration part up to $x_{Ag} = 0{,}622$ in the temperature range up to 1273 K, are presented in Table 4. Beside detected liquidus temperatures for all investigated samples, there are also two characteristic temperatures detected - one at 696 K, which occurs in the samples A2-A7, and the other one at 718 K, occurring in the samples A2 - A5.

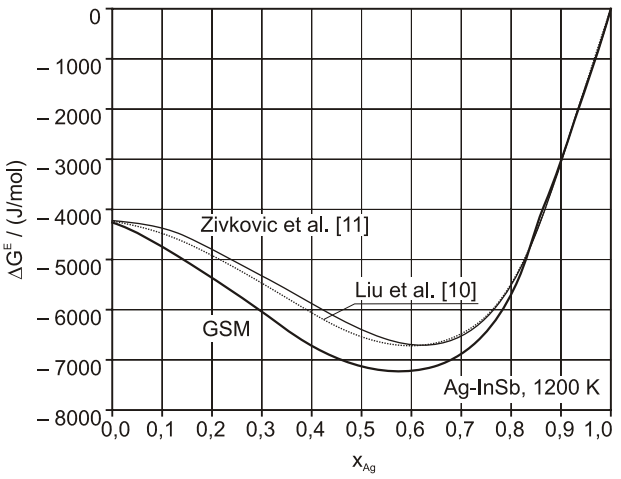

Figure 4. **Comparison of the calculated results with literature data [10, 11]**

Slika 4. **Usporedba proračunatih rezultata s literaturnim vrijednostima [10, 11]**

SEM images for the samples A3 and A5, as well as optic microphotographs for the sample A2, are shown in Figure 5.

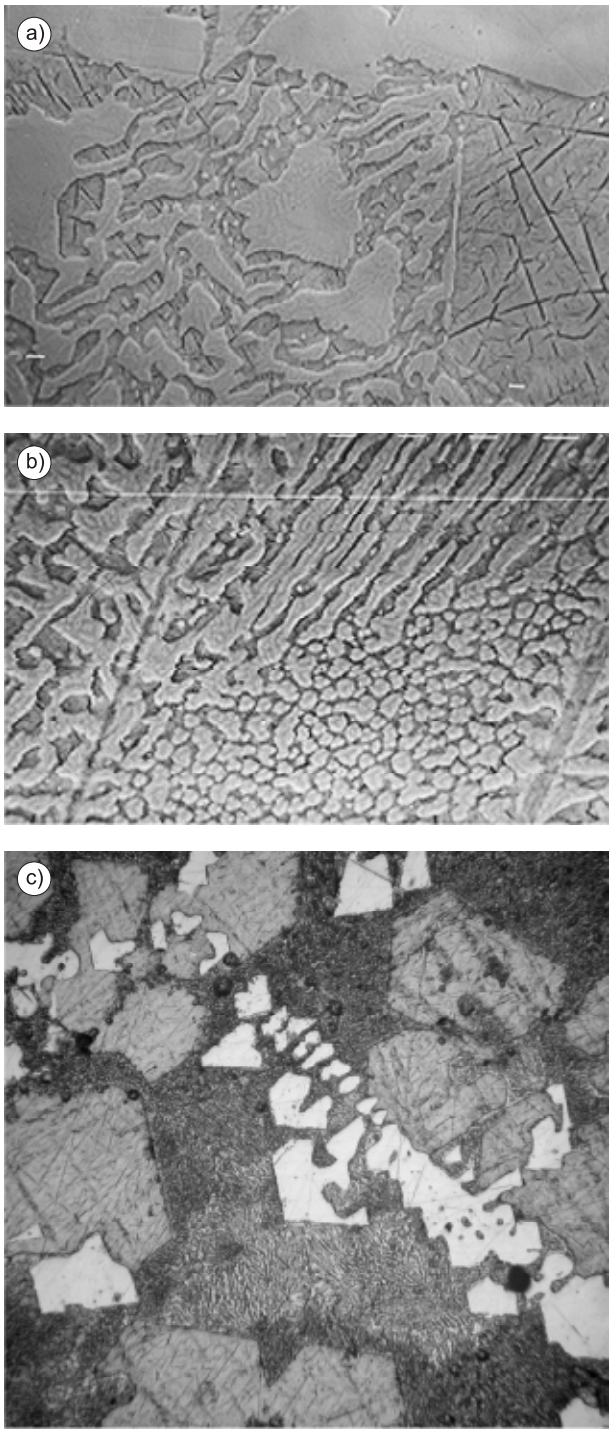

Figure 5. **SEM images of the investigated samples A3 a) (enlargement 1000×) and A5 b) (enlargement 1500×) and optic microphotograph of sample A2 c) (enlargement 300×)**

Slika 5. **SEM fotografije ispitivanih uzoraka A3 a) (povećanje 1000×), A5 b) (povećanje 1500×) i optička mikrofotografija uzorka A2 c) (povećanje 300×)**

Microstructure analysis of the sample A2 and A3 (Figure 5.a, c) shows structure of primary solidified indium-antimonide, occurring in the form of poliedric crystals

Table 4. **Characteristic temperatures detected by DTA for the concentration part of Ag-InSb system up to $x_{Ag} = 0,622$**
Tablica 4. **Karakteristične temperature određene primjenom DTA u Ag-In-Sb sustavu u opsegu koncentracija do $x_{Ag} = 0,622$**

Sample	x_{Ag}	T / K	
		Liquidus temperatures	Other temperatures
A1	0	798	/
A2	0,109	773	696, 717
A3	0,215	758	697, 719
A4	0,319	743	696, 718
A5	0,422	723	696, 718
A6	0,523	733	697, 703
A7	0,622	863	696

surrounded by the eutectic. Other present, white phase is probably related to the Ag_2In (Figure 5.c). Deformation lines, which may be well seen in Figure 5.a, are typical for antimony-based intermetallic compounds and are caused usually by elongation during solidification. Isothermal solidification of the eutectic type (Figure 5.b) could be supposed according to the structure of the sample A5.

The results of XRD for the samples A5 and A7 were presented in Table 5.

Table 5. **XRD results for the investigated samples A5 and A7**
Tablica 5. **XRD rezultati za ispitivane uzorke A5 i A7**

A5 nm	x_{Ag} = 0,422	A7 nm	x_{Ag} = 0,622
0,6437		0,6461	
0,3780		0,4032	
0,3535	InSb	0,3086	Sb
0,3253		0,2669	
0,3116	Sb	0,2581	Ag-In, Ag-Sb
0,2829		0,2403	Ag-In, Ag-Sb
0,2699	InSb	0,2272	Ag-In, Ag-Sb
0,2586	Ag-In, Ag-Sb	0,2146	Sb
0,2404	Ag-In, Ag-Sb	0,1954	
0,2277	Ag-In, Ag-Sb	0,1872	Sb
0,2146	Sb	0,1759	Ag-In, Ag-Sb
0,2063	InSb	0,1551	
0,1928		0,1486	Ag-In, Ag-Sb
0,1869	Sb	0,1411	Sb
0,1762	Ag-In, Ag-Sb	0,1360	Ag-In, Ag-Sb
0,1546			
0,1490	Ag-In, Ag-Sb		
0,1409	Sb		
0,1362	Ag-In, Ag-Sb		

The identification was done only using available ASTM reflections for the constituent metals and binary systems in the ternary Ag-In-Sb system [39]. Therefore, obtained results could be partially used for the determination of the investigated alloys composition, because some unidentified peaks in the recorded difractograms may be due to the possible existence of some ternary phases occurring in the system.

Based on the results of experimental investigations of the chosen samples, phase diagram for the low-temperature part of the Ag-InSb system was constructed (Figure 6.) and compared with literature data [5].

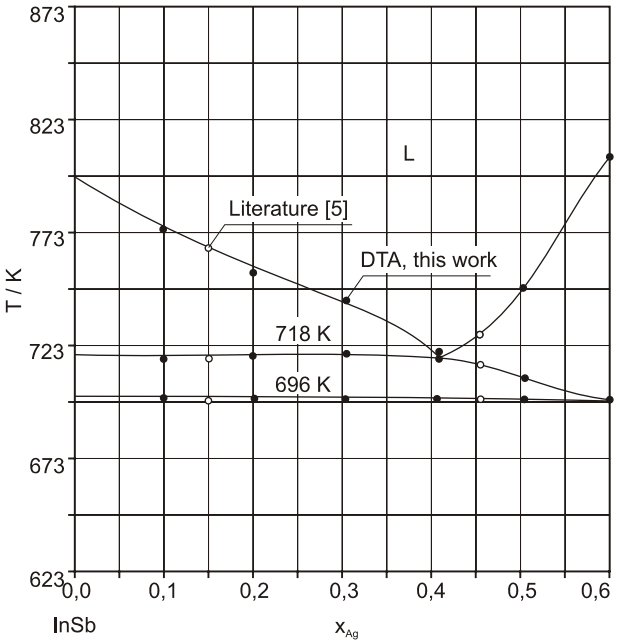

Figure 6. **Proposed phase diagram of the Ag-In-Sb system in the concentration range up to $x_{Ag} = 0,622$**
Slika 6. **Predloženi fazni dijagram Ag-In-Sb sustava u intervalu koncentracija do $x_{Ag} = 0,622$**

The accordance with available referent data, both experimental [5], and calculated recently [7, 10], may be confirmed.

CONCLUSIONS

According to the investigations of thermodynamic and structural properties of the alloys in the Ag-InSb system, presented in this paper, following observations could be made:

1. Thermodynamic calculation was done according to the general solution model. Obtained values for integral molar excess Gibbs energies are uniform, having negative values in the whole composition range in the investigated temperature interval from 1000 to 1200K and showing minimum values of about –6 kJ/mol at the equiatomic

concentration. Activity values for silver exhibits negative deviation from Raoult law, indicating good miscibility between the constituent components. Also, symmetric thermodynamic behavior of Ag-InSb alloys was determined by Chou's similarity coefficient concept.

2. Characterization of the investigated samples in the Ag-InSb was done using DTA, XRD, SEM and optic microscopy. Based on obtained data, phase diagram for the selected part of the Ag-InSb system up to x_{Ag}=0.622 was proposed.

Finally, presented thermodynamic data for the Ag-In-Sb alloys could be useful for the further assessment of this system and interpretation of the phenomena occurring in the multicomponent lead-free systems based on silver.

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