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PREDICTING OF THERMODYNAMIC PROPERTIES OF TERNARY Au-In-Sb SYSTEM

MODELOWANIE WŁAŚCIWOŚCI TERMODYNAMICZNYCH W UKŁADZIE Au-In-Sn

The results of thermodynamic predicting applied on the ternary Au-In-Sb system, one of potencial lead-free solders, are presented in this paper. The general solution model has been used to predict the thermodynamic properties in wide temperature range from 873-1673K, based on which ternary interaction coefficient was determined using Mathematical Modeling System (MLAB).

Keywords: Ternary system Au-In-Sb, General solution model, Ternary interaction coefficient, Lead-free solders

W pracy przedstawiono modelowanie właściwości termodynamicznych układu Au-In-Sb, który może rozpatrywany jako kandydat dla lutowi bezołowiowych. Zastosowano ogólny model stosowany dla roztworów celem przewidywania właściwości termodynamicznych w szerokim zakresie temperatur 873 K – 1673 K. W modelu tym, trójskładnikowy parametr oddziaływania został wyznaczony za pomocą Mathematical Modeling System (MLAB).

1. Introduction

Gold and gold alloys are widely applied in modern technical branches – electronics, communications, space and aero technologies, chemistry and medical science, etc. They are known for good mechanical and thermal properties, as well as corrosion resistance. Owing to formation of low temperature eutectic with other elements, gold alloys are often used as welding alloys in electronics [1]. In-based alloys may be a possible alternative to conventional Pb-based solders in step soldering. Also, the phase diagram of ternary Au-In-Sb system is of importance in predicting the interface reactions between In-based lead-free solders and Au-substrate which can provide a tool for design a potencial interface [2]. Literature thermodynamic data for constitutive binary systems, Au-In, In-Sb and Au-Sb can be found in the COST 531 Database for Lead Free Solders[3]. So far, some thermodynamic information about ternary system Au-In-Sb and phase equilibria investigation of this system were given by Kubiak and Schubert [4] and Tsai and Wiliams [5].

2. Theoretical fundamentals

There are many methods for calculation thermodynamic properties of ternary system based on information about constitutive binary systems. Chou's general solution model [6] has been proved to be most reasonable one in all aspects among available geometrical models. This model breaks down boundaries between symmetrical and asymmetrical systems and generalizes various kind of situations, but also completely exclude any human interference in the calculation process. Precision of this model has already been proved theoretically and the accuracy of calculation has also been shown in some practical examples [7]. Therefore, this model is used for calculating the thermodynamic properties of Au-In-Sb ternary system. The basic equation of the general solution model is given as follows:

$$\Delta G^E = x_1 x_2 \Delta G^E_{12} + x_2 x_3 \Delta G^E_{23} + x_1 x_3 \Delta G^E_{31} + x_1 x_2 x_3 f_{123}, \quad (1)$$

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where:

$$\Delta G_{ij}^{E} = X_i X_j (A_{ij}^{0} + A_{ij}^{1}(X_i - X_j) + A_{ij}^{2}(X_i + X_j)^2 + \\ + \ldots + A_{ij}^{n}(X_i - X_j)^n) \quad (2)$$

and A_{ij}^{0}, A_{ij}^{1}, A_{ij}^{2} are parameters for binary system "ij" (analogue to the Redlich-Kister parameters) which can be temperature dependent; X_i and X_j are the mole fractions of component "i" and "j" in "ij" binary system; f_{123} is ternary interaction coefficient, expressed as:

$$f_{123} = (2\xi_{12} - 1)\{A_{12}^{2}((2\xi_{12} - 1)x_3 + 2(x_1 - x_2)) + A_{12}^{1}\} + \\ + (2\xi_{23} - 1)\{A_{23}^{2}((2\xi_{23} - 1)x_1 + 2(x_2 - x_3)) + A_{23}^{1}\} + \\ (2\xi_{31} - 1)\{A_{31}^{2}((2\xi_{31} - 1)x_2 + 2(x_3 - x_1)) + A_{31}^{1}\} \quad (3)$$

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

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

where:

$$\eta_I = \int_0^1 (\Delta G_{12}^{E} - \Delta G_{13}^{E})^2 dX_1 \\ \eta_{II} = \int_0^1 (\Delta G_{21}^{E} - \Delta G_{23}^{E})^2 dX_2 \quad (5) \\ \eta_{III} = \int_0^1 (\Delta G_{31}^{E} - \Delta G_{32}^{E})^2 dX_3$$

and

$$X_{1(12)} = x_1 + x_3\xi_{12}; X_{2(23)} = x_2 + x_1\xi_{23}; X_{3(31)} = x_3 + x_2\xi_{31}. \quad (6)$$

with a temperature dependence taken as

$$L_{123}^{v} = a^{v} + b^{v} \cdot T(v = 0, 1, 2), \quad (7)$$

where L_{ijk}^{v} are the Redlich-Kister parameters for the ternary system ijk; and x_i – mole fraction of the component i.

In all above-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 the respective components in the investigated ternary system.

3. Results and discussion

For the purpose of further calculation, basic thermodynamic information on the constitutive subsystems in the Au-In-Sb system were taken from Refs. [3], and presented in the form of Redlich-Kister parameters in Table 1.

Ternary Au-In-Sb system has been investigated in 9 sections. Three sections were taken from Au, In and Sb corner, respectively, with following ratios 1:3, 1:1, 3:1, and with molar content of 0–0.9 for the third component. The values of Redlich-Kister coefficients, from Tab.1 and previously specified Eqs. (4) and (5), were used for the calculation of similarity coefficients and deviation sum of squares. The obtained results (average values) are given in Table 2.

TABLE 1

Redlich-Kister parameters for the investigated systems

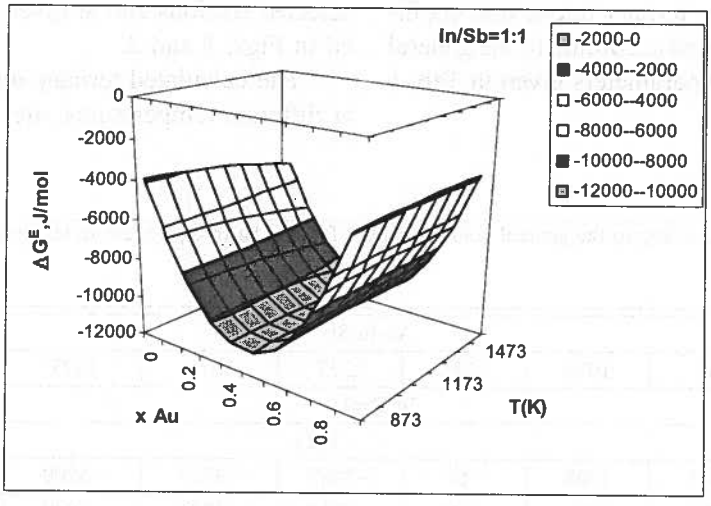
System ij	L_{ij}^{o} (T)	L_{ij}^{1} (T)	L_{ij}^{2} (T)
Au-In [3]	−80027.7 + 7173262T − 9.57049TlnT	− 34977.3 + 117.293782T − 13.0337TlnT	0
In-Sb [3]	− 25631.2 + 102.9324T − 13.45816TlnT	− 2115.4 − 1.31907T	2908.9
Au-Sb [3]	−15437.35 − 4.63455T	− 18854.1 + 15.64707T	− 4271.85

TABLE 2

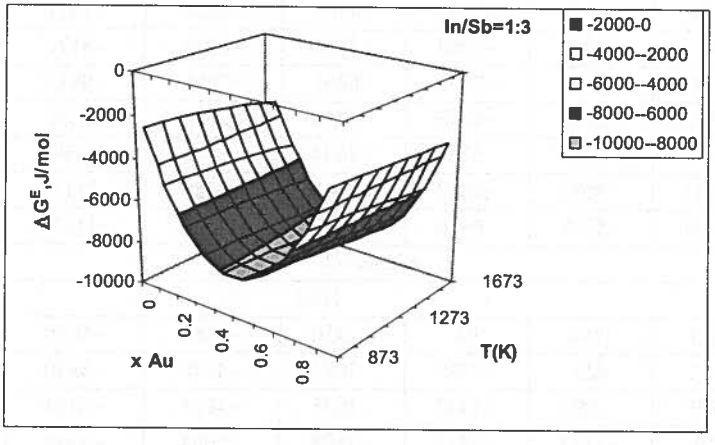
Similarity coefficients and deviation sum of squares

Deviation sum of squares		
η_I	η_{II}	η_{III}
33300000	44400000	1075536
Similarity coefficient		
ξ_{AuIn}	ξ_{InSb}	ξ_{AuSb}
0.428308	0.974429	0.033831

a)



b)



c)

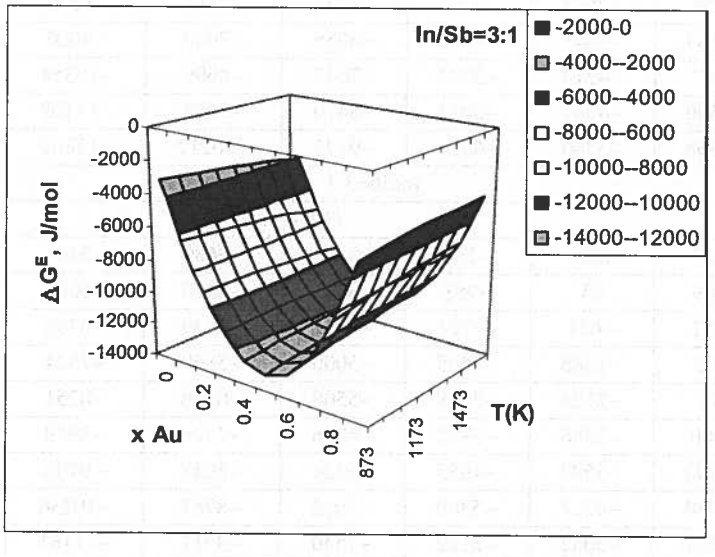


Fig. 1. Results of ΔG^E calculation according to the general solution model for the Au-In-Sb system in temperature interval 873–1673 K (the sections with In/Sb molar ratio equal to: a) – 1/1, b) – 1/3 and c) – 3/1)

The calculation was done in the temperature interval from 873 to 1673 K. The values for the integral Gibbs excess energies, ΔG^E, and the ternary interaction coefficients, f_{123}, have been calculated according to the general solution model, based on the parameters given in Tab. 1 and Eqs. (1, 3), respectively.

The calculated integral molar Gibbs excess energies (ΔG^E) of the investigated system Au-In-Sb, along selected sections and at given temperatures, are presented in Figs. 1 and 2.

The calculated ternary interaction coefficients, f_{123}, at different temperatures, are presented in Tabs. 3.

TABLE 3

Results of f_{123} calculation according to the general solution model for the Au-In-Sb system in temperature interval 873–1673 K

a) sections from gold corner

Au-In-Sb									
T, K	873	973	1073	1173	1273	1373	1473	1573	1673
In:Sb=1:1									
xAu	f123								
0	4505	3431	1008	−80	−2467	−3533	−5209	−6826	−8511
0.1	3743	2673	254	−831	−3214	−4278	−5949	−7563	−9243
0.2	2982	1915	−500	−1582	−3961	−5022	−6690	−8300	−9974
0.3	2221	1158	−1254	−2333	−4707	−5766	−7431	−9036	−10705
0.4	1460	400	−2008	−3084	−5454	−6510	−8172	−9773	−11437
0.5	699	−358	−2762	−3835	−6201	−7255	−8912	−10510	−12168
0.6	−63	−1115	−3516	−4586	−6948	−7999	−9653	−11246	−12899
0.7	−824	−1873	−4270	−5337	−7694	−8743	−10394	−11983	−13631
0.8	−1585	−2631	−5024	−6087	c8441	−9488	−11135	−12720	−14362
0.9	−2346	−3388	−5779	−6838	−9188	−10232	−11875	−13457	−15093
In:Sb=1:3									
xAu	f123								
0	4725	3635	1196	94	−2310	−3387	−5076	−6709	−8257
0.1	3942	2857	423	−674	−3073	−4146	−5830	−7457	−8999
0.2	3158	2079	−350	−1442	−3835	−4905	−6584	−8206	−9741
0.3	2375	1301	−1123	−2211	−4598	−5664	−7338	−8954	−10482
0.4	1592	523	−1895	−2979	−5360	−6423	−8092	−9703	−11224
0.5	809	−256	−2668	−3747	−6123	−7181	−8846	−10451	−11966
0.6	25	−1034	−3441	−4516	−6885	−7940	−9600	−11199	−12708
0.7	−758	−1812	−4214	−5284	−7647	−8699	−10354	−11948	−13449
0.8	−1541	−2590	−4987	−6053	−8410	−9458	−11108	−12696	−14191
0.9	−2324	−3368	−5760	−6821	−9172	−10217	−11862	−13445	−14933
In:Sb=3:1									
xAu	f123								
0	4285	3227	820	−254	−3475	−3680	−5341	−6943	−8457
0.1	3545	2489	85	−988	−3983	−4410	−6069	−7668	−9179
0.2	2806	1752	−651	−1721	−4492	−5139	−6796	−8393	−9901
0.3	2067	1015	−1386	−2455	−5000	−5869	−7524	−9118	−10623
0.4	1328	278	−2121	−3188	−5508	−6598	−8251	−9843	−11344
0.5	589	−460	−2856	−3922	−6016	−7328	−8979	−10568	−12066
0.6	−151	−1197	−3592	−4655	−6524	−8058	−9706	−11293	−12788
0.7	−890	−1934	−4327	−5389	−7032	−8787	−10434	−12018	−13509
0.8	−1629	−2671	−5062	−6122	−7540	−9517	−11161	−12743	−14231
0.9	−2368	−3409	−5797	−6856	−8048	−10247	−11889	−13468	−14953

b) sections from indium corner

Au-In-Sb									
T, K	873	973	1073	1173	1273	1373	1473	1573	1673
Au:Sb=1:1									
xIn	f123								
0	919	−153	−2574	−3660	−6044	−7108	−8780	−10392	−11916
0.1	1233	164	−2254	−3337	−5718	−6780	−8449	−10059	−11580
0.2	1548	482	−1933	−3014	−5391	−6452	−8119	−9726	−11244
0.3	1862	799	−1612	−2691	−5065	−6124	−7788	−9393	−10908
0.4	2177	1117	−1292	−2368	−4739	−5796	−7457	−9060	−10572
0.5	2492	1435	−971	−2045	−4412	−5467	−7127	−8727	−10237
0.6	2806	1752	−651	−1721	−4086	−5139	−6796	−8393	−9901
0.7	3121	2070	−330	−1398	−3760	−4811	−6466	−8060	−9565
0.8	3435	2387	−9	−1075	−3433	−4483	−6135	−7727	−9229
0.9	3750	2705	311	−752	−3107	−4155	−5804	−7394	−8893
Au:Sb=1:3									
xIn	f123								
0	2932	1843	−595	−1696	−4099	−5174	−6862	−8492	−10036
0.1	3045	1961	−472	−1569	−3967	−5039	−6723	−8349	−9889
0.2	3158	2079	−350	−1442	−3835	−4905	−6584	−8206	−9741
0.3	3272	2197	−227	−1316	−3703	−4770	−6445	−8062	−9593
0.4	3385	2315	−104	−1189	−3572	−4635	−6307	−7919	−9445
0.5	3498	2433	18	−1062	−3440	−4500	−6168	−7776	−9297
0.6	3611	2551	141	−936	−3308	−4366	−6029	−7633	−9149
0.7	3725	2669	264	−809	−3176	−4231	−5890	−7490	−9001
0.8	3838	2787	386	−682	−3044	−4096	−5751	−7347	−8853
0.9	3951	2905	509	−556	−2913	−3961	−5613	−7204	−8705
Au:Sb=3:1									
xIn	f123								
0	−1094	−2150	−4553	−5625	−7989	−9042	−10698	−12293	−13795
0.1	−579	−1632	−4035	−5105	−7469	−8521	−10176	−11769	−13271
0.2	−63	−1115	−3516	−4586	−6948	−7999	−9653	−11246	−12748
0.3	453	−598	−2998	−4066	−6427	−7478	−9131	−10723	−12224
0.4	969	−81	−2479	−3546	−5906	−6956	−8608	−10200	−11700
0.5	1485	437	−1961	−3027	−5385	−6434	−8086	−9677	−11176
0.6	2001	954	−1442	−2507	−4864	−5913	−7564	−9154	−10653
0.7	2517	1471	−924	−1988	−4343	−5391	−7041	−8630	−10129
0.8	3033	1988	−405	−1468	−3822	−4870	−6519	−8107	−9605
0.9	3549	2505	113	−948	−3302	−4348	−5996	−7584	−9081

c) sections from antimony corner

Au-In-Sb									
T, K	873	973	1073	1173	1273	1373	1473	1573	1673
Au:In=1:1									
xSb	f123								
0	478	−562	3863	−4009	−6358	−7401	−9045	−10627	−12116
0.1	925	−122	4292	−3581	−5937	−6985	−8635	−10223	−11720
0.2	1372	319	4722	−3153	−5517	−6569	−8225	−9820	−11324
0.3	1818	759	5151	−2726	−5096	−6153	−7815	−9416	−10928
0.4	2265	1199	5581	−2298	−4676	−5737	−7404	−9013	−10532
0.5	2712	1639	6010	−1870	−4256	−5321	−6994	−8609	−10137
0.6	3158	2079	6440	−1442	−3835	−4905	−6584	−8206	−9741
0.7	3605	2519	6869	−1014	−3415	−4488	−6174	−7802	−9345
0.8	4052	2959	7298	−587	−2994	−4072	−5764	−7398	−8949
0.9	4498	3399	7728	−159	−2574	−3656	−5354	−6995	−8553
Au:In=1:3									
xSb	f123								
0	2271	1231	−1159	−2219	−4569	−5614	−7259	−7503	−10337
0.1	2539	1491	−905	−1970	−4328	−5377	−7028	−7269	−10119
0.2	2806	1752	−651	−1721	−4086	−5139	−6796	−7036	−9901
0.3	3074	2013	−396	−1473	−3845	−4902	−6565	−6803	−9683
0.4	3341	2274	−142	−1224	−3603	−4664	−6333	−6569	−9465
0.5	3608	2535	112	−975	−3361	−4427	−6101	−6336	−9247
0.6	3876	2796	367	−726	−3120	−4190	−5870	−6103	−9029
0.7	4143	3056	621	−477	−2878	−3952	−5638	−5869	−8811
0.8	4410	3317	875	−229	−2637	−3715	−5407	−5636	−8593
0.9	4678	3578	1130	20	−2395	−3477	−5175	−5403	−8375
Au:In=3:1									
xSb	f123								
0	−1315	−2354	−4741	−5799	−8146	−9189	−10831	−12410	−13895
0.1	−689	−1734	−4129	−5192	−7547	−8594	−10242	−11828	−13322
0.2	−63	−1115	−3516	−4586	−6948	−7999	−9653	−11246	−12748
0.3	563	−496	−2904	−3979	−6348	−7404	−9064	−10664	−12174
0.4	1189	123	−2291	−3372	−5749	−6809	−8476	−10083	−11600
0.5	1815	743	−1679	−2765	−5150	−6214	−7887	−9501	−11026
0.6	2441	1362	−1066	−2158	−4551	−5620	−7298	−8919	−10452
0.7	3067	1981	−454	−1552	−3951	−5025	−6710	−8337	−9878
0.8	3693	2600	159	−945	−3352	−4430	−6121	−7755	−9305
0.9	4319	3220	771	−338	−2753	−3835	−5532	−7173	−8731

The values of the ternary interaction coefficients for the liquid phases of the investigated systems, calculated using general solution model, were further used in determination of the ternary interaction parameters, L^{v}_{ijk}, according to Eqs. (7, 8). Therefore, MLAB software [9] was applied to the process of fitting (Table 4).

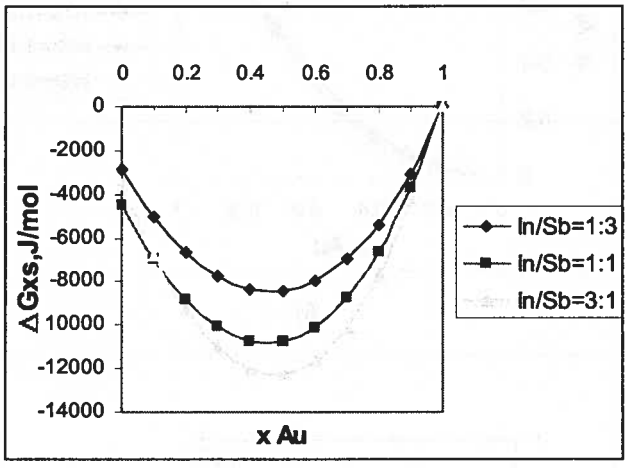
TABLE 4

Ternary interaction parameters, L^{v}_{ijk}, obtained using MLAB software for the Au-In-Sb system

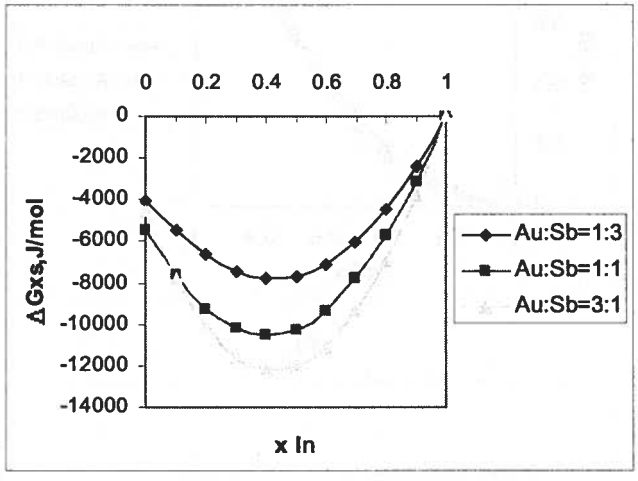
System *ijk*	L^{o}_{ijk} (T)	L^{1}_{ijk} (T)	L^{2}_{ijk} (T)
Au-In-Sb	1129.0976 − 16.232T	18074.6295 − 15.969T	20537.8775 − 17.185T

In order to give beter description of data calculated using general solution model, at Fig. 2 and 3, respectively, are presented dependence of integral molar excess Gibbs energy and activity on composition at temperature of 1373 K.

a)



b)



c)

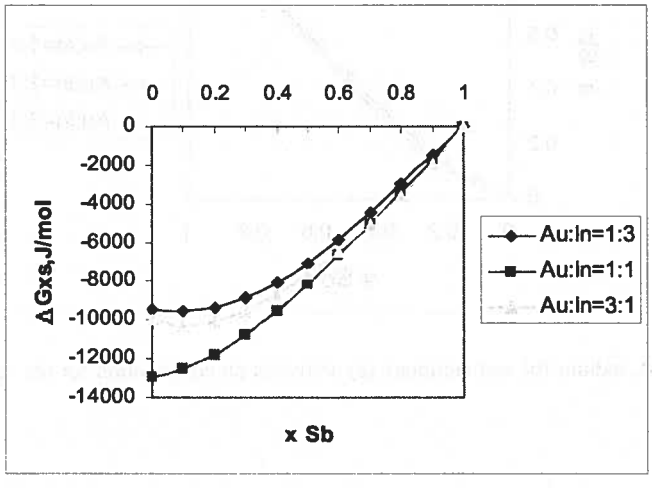
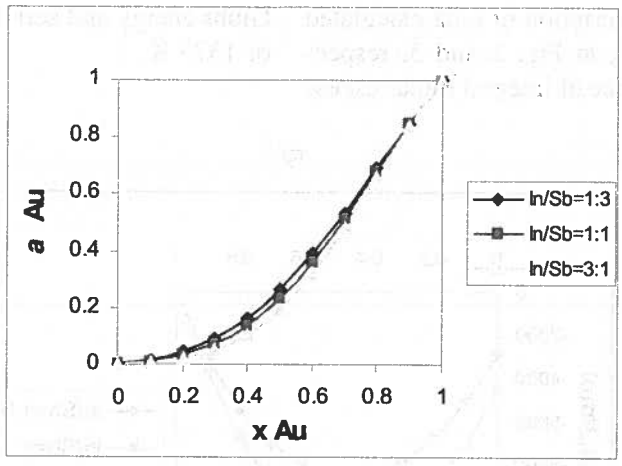
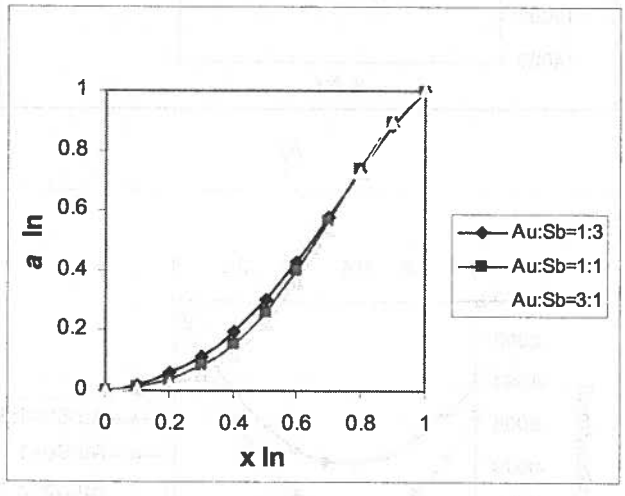


Fig. 2. Dependence of ΔG^E on composition for the Au-In-Sb system at 1373 K, along the sections from: a) – gold corner, b)- - indium corner and c) – antimony corner

a)



b)



c)

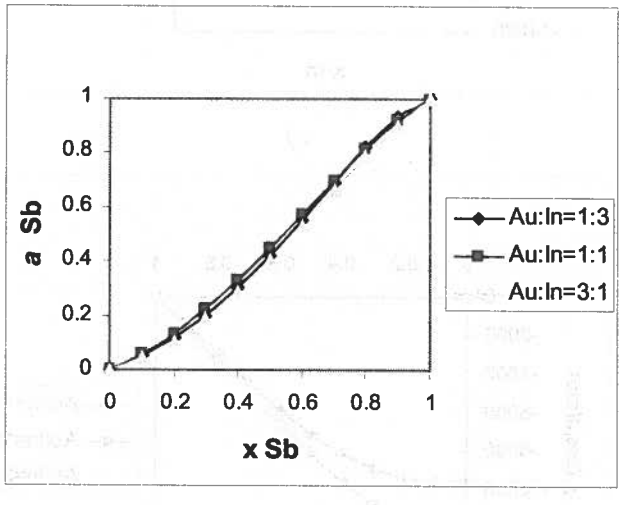


Fig. 3. Dependence of gold (a), indium (b) and antimony (c) activities on composition for the Au-In-Sb system at 1373 K

Although the common way to obtain the ternary interaction parameters is the optimization based on the experimental data from literature, it could be also done using the estimation method, without applying experimental data. Similar procedure was presented recently in literature [10], too.

The results for the Au-In-Sb system, presented here, could be taken as a contribution to the better knowledge of that ternary system, which, until now, has not been completely investigated from the thermodynamic point of view.

4. Conclusions

Calculation of thermodynamic properties of the Au-In-Sb system was done using the general solution model, and Redlich-Kister ternary interaction parameters were obtained in the temperature interval from 873 to 1673 K. Results obtained in this work contributes to more complete knowledge of thermodynamic properties of Au-In-Sb alloys and may be used for the calculation of the ternary phase diagram of this system, which is interesting for detailed research as a possible lead-free solder.

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