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PHASE RELATIONS NEAR TERNARY EUTECTIC POINT IN THE Ag-In-Sb SYSTEM

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Abstract

The results of the phase relations near ternary eutectic point in the Ag-In-Sb system are investigated in this paper. Phase equilibrium calculation was done using Thermocalc software and experimental DTA results for the chosen alloys in the isopleths with molar ration of In:Sb = 7:3; 9:1 and 1:1. The structural characteristics of these alloys have been investigated using light optic microscopy and scanning electron microscopy, while hardness measurements have also been done. Solidification path for three ternary alloys located on three different investigated isopleths was calculated using Pandat software.

Keywords: lead-free solders, phase equilibria, ternary systems, Ag-In-Sb alloys

1. Introduction

A need for a substitution of conventional lead-bearing solders stimulated widespread search for new lead-free materials, which can be used in automotive, avionics and electronic industry. As a response to NCSM Lead-Free Soldering Project in the United States [1] as well as JEIDA and JWES projects carried out in Japan [2], European Union created COST 531 Action, which main aim was to choose possible candidates for lead-free solders among several groups of alloys. It was soon established that the group of silver-based alloys with the additions of low-melting metals like Sn, Bi or In can be a

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good substitute for idustrial application. However, to adjust solidification temperature as well as the structure and mechanical properties of the joint, a wide range of other metals can be introduced into the alloy as a third component.

Investigations of antimony addition to Ag-In system has been recently carried out by Buchtova et al. [3] and Živković et al. [4,5] Isothermal section of this system at 200^{o} C was experimentally determined, as well as the isophlet for the ratio of In : Sb = 1. In order to find out how the antimony addition will influence the temperature of the eutectic point in the binary Ag-In system and how phase relations after this addition may look like, the particular part of the ternary system with low Sb content was investigated in this work. Next, using previously optimized parameters [6] these results were compared with the phase relations derived from computer calculations.

2. Experimental procedure

The samples, of chosen alloys along the investigated sections with molar ratio of In:Sb equal to 7:3, 9:1 (the compositions and masses are presented in Table 1) and 1:1 (sample with 10, 20 and 40 wt%Ag), were prepared from Ag, In and Sb of 99.99% purity. The samples were prepared in an induction furnace under inert gas atmosphere, where an extra amount of antimony (about 2-3%) was added to compensate the weight loss due to the volatilization of antimony.

Differential thermal analysis (DTA) was performed using Derivatograph (MOM, Budapest). The experiments were carried out with the heating rate $10\ ^{o}$/min, using sintered Al_2O_3 as the reference specimen.

Light optic microscopy was performed at Reichert MeF_2 microscope, using concentrated H_2O_2 or solution of ($32gFeCl_3$+$100ml H_2O_2$+$100ml H_2O$) as etching reagents, while scanning electron microscopy (SEM) was Performed at JEOL/JSM T20 scanning microscope.

X-ray diffraction (XRD) analysis was carried out using X-ray difractometer (Siemens), with Cu anticathode and Ni filters (2θ in range 4-68, intensity in range from 0-600/800).

Standard apparatus for Vickers hardness measurements was used in this kind of experiments.

3. Results and Discussion

3.1. Phase equilibrium determination

Differential thermal analysis (DTA) was performed on samples along two isophlets determined by In:Sb ratio 9:1 and 7:3, respectively, and the obtained results are gathered in Table 2. The evolution of phase equilibria with antimony addition, starting from binary Ag-In system (Fig.1a), is shown in subsequent Figures 1a through 1d. In Figure 1d the isophlet for the ratio In:Sb =1:1, determined previously [3,4], is also shown for comparison. The results demonstrate the change of the position of the eutectic point with the increase of antimony content.

The Ag-In-Sb system consists of the following phases [7]: FCC_A1 - solid solution based on silver, HCP_A3 - which continuously exists from the Ag-In side to the Ag-Sb side in the ternary Ag-In-Sb system, ZINCBLENDE_B3 - phase based on In and Sb as the main constituents in almost equiatomic composition,

Table 1. The composition and masses of chosen alloys in the investigated sections with molar ratio of In:Sb equal to 7:3 (a) and 9:1 (b)

a)

Section with molar ratio In:Sb=7:3						
xAg	xIn	xSb	wt%Ag	wt%In	wt%Sb	sample mass, g
0,1	0,63	0,27	9,2993	62,3613	28,3394	2,1971
0,2	0,56	0,24	18,7445	55,8673	25,3882	2,2686
0,3	0,49	0,21	28,3392	49,2705	22,3904	2,3461
0,4	0,42	0,18	38,0868	42,5685	19,3447	2,4305
0,5	0,35	0,15	47,9910	35,7588	16,2502	2,5226
0,6	0,28	0,12	58,0558	28,8388	13,1054	2,6238

b)

Section with molar ratio In:Sb=9:1						
xAg	xIn	xSb	wt%Ag	wt%In	wt%Sb	sample mass, g
0,1	0,81	0,09	9,4004	81,051	9,5491	2,2378
0,2	0,72	0,08	18,9269	72,528	8,5451	2,3080
0,3	0,63	0,07	28,5820	63,891	7,5274	2,3839
0,4	0,54	0,06	38,3684	55,1357	6,4959	2,4661
0,5	0,45	0,05	48,2888	46,2609	5,4503	2,5554
0,6	0,36	0,04	58,3459	37,2638	4,3903	2,6528

TETRAGONAL_A6 - phase based on indium, RHOMBOEDRAL_A7 - phase based on antimony, AGSB_ORTHO - phase based on silver and antimony, intermediate stoichiometric compounds Ag_2In and $AgIn_2$, and the liquid phase.

Using the thermodynamic description of the ternary system, which was worked out in our earlier paper [6], the respective isopleths were calculated using ThermoCalc software and were compared with the experimental DTA results, as shown in Figures 1a - 1d.

It was found that the calculated ternary eutectic point occurs at temperature of 414,9K at the composition equal to X_{Ag} = 0,014 and X_{Sb} =0,017 mole fractions. So, isothermal sections just above and below ternary eutectic temperature were calculated using Pandat [8] software and are shown in Fig.2a and 2b.

The existence of calculated ternary eutectic point has been checked experimentally, using DTA and metallography, as shown in Fig.3. The eutectic structure was proven and the eutectic temperature of 419.5K (or 146.5^{o}C) was obtained, which is in accordance with the value predicted by calculation. Also, this is in agreement with literature data presented in [9], in which the ternary eutectic in the Ag-In-Sb system is given at the temperature of 417K (or 144^{o}C).

3.2. Structural characteristics of the alloys

In order to find out how the solidification process of the alloy may depend on antimony addition, some of the alloys in the investigated sections were investigated using

Table 2. DTA results obtained for investigated sections in the Ag-In-Sb system

Alloy	Results of measurments	H_V average
10wt%Ag (molar ratio In:Sb=1:1)	101, 102, 103	102
20wt%Ag (molar ratio In:Sb=1:1)	117, 118, 119	118
40wt%Ag (molar ratio In:Sb=1:1)	133, 140	137
50wt%Ag (molar ratio In:Sb=7:3)	109, 109, 110	109
40wt%Ag (molar ratio In:Sb=9:1)	165, 145	155

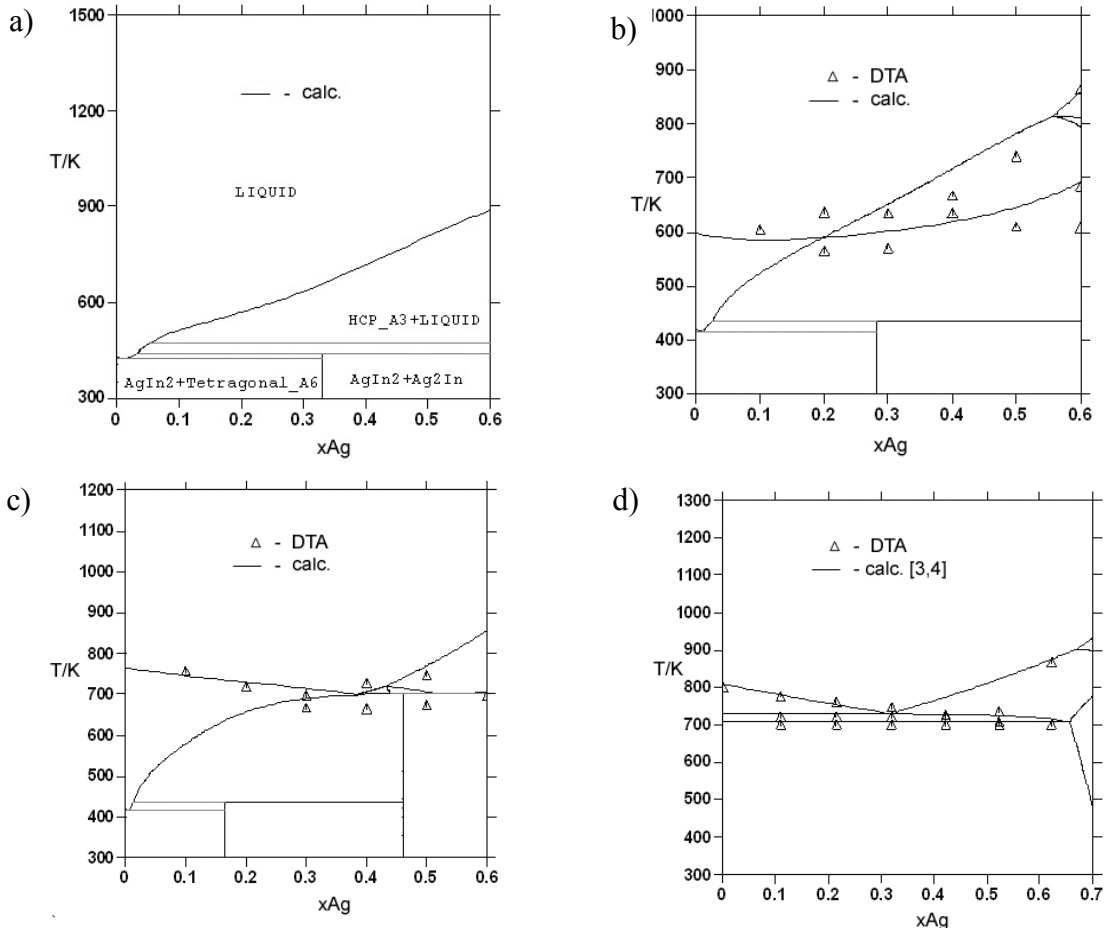


Fig. 1. Binary Ag-In system (a); Isopleth for X_{In}/X_{Sb}=9:1 (b); Isopleth for X_{In}/X_{Sb}=7:3 (c); Isopleth for X_{In}/X_{Sb}=1:1 (d)

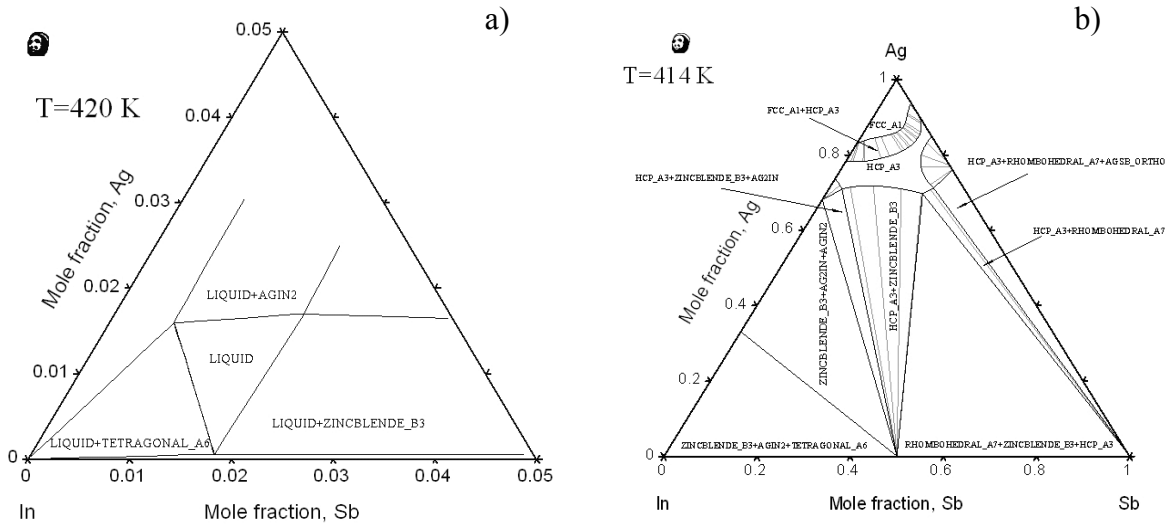


Fig.2. a) Isothermal section of the ternary system at T =420 K; b) Isothermal section of the ternary system at T =414 K

light optic microscopy (Fig.4), scanning electron microscopy (Fig.5) and X-ray diffraction analysis (Table 3).

Reasonable agreement between the experimental data (LOM, SEM and XRD) and the results of calculations in the field near ternary eutectic point in the In-rich part of the investigated system was found.

3.3. Calculation of the solidification path

Solidification path for three ternary alloys located on three different isophlets, and investigated by metallographic and SEM methods was calculated using Pandat software [8]. Scheil model of the alloy solidification was used during these calculations. The obtained results for three different solidification paths are shown in Fig.6. Depending on In/Sb ratio different three-phase equilibrium is obtained at the end of the solidification process, which is in accordance to obtained experimental data.

3.4. Hardness measurements

Hardness tests of alloys chosen from three different investigated isopleths were

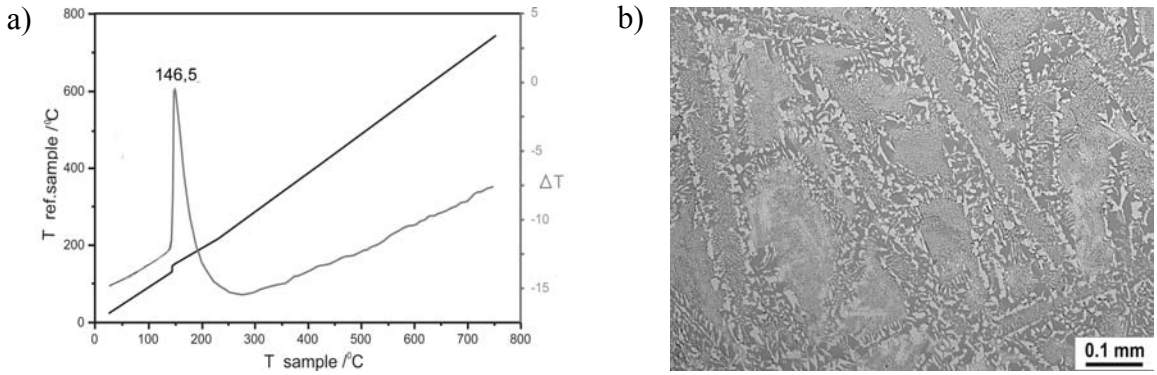


Fig.3. DTA (a) and microphotograph (b) of the ternary eutectic point

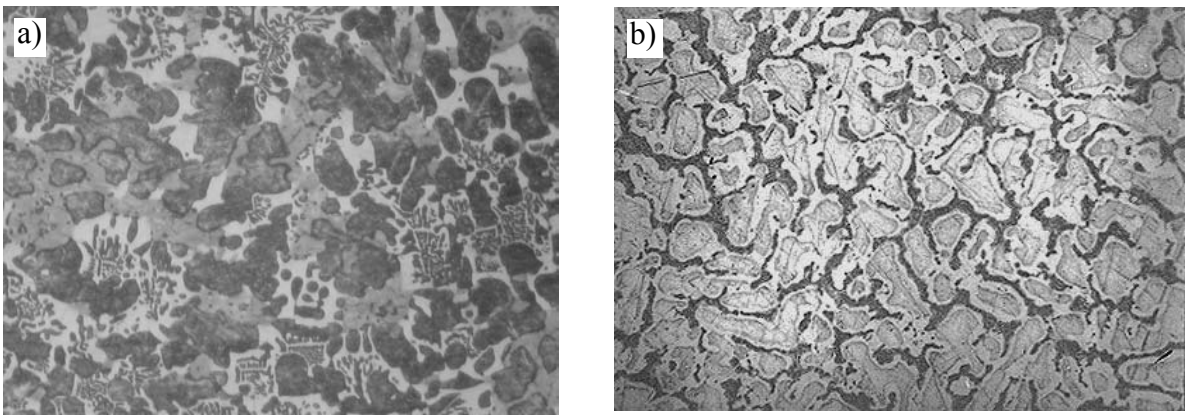
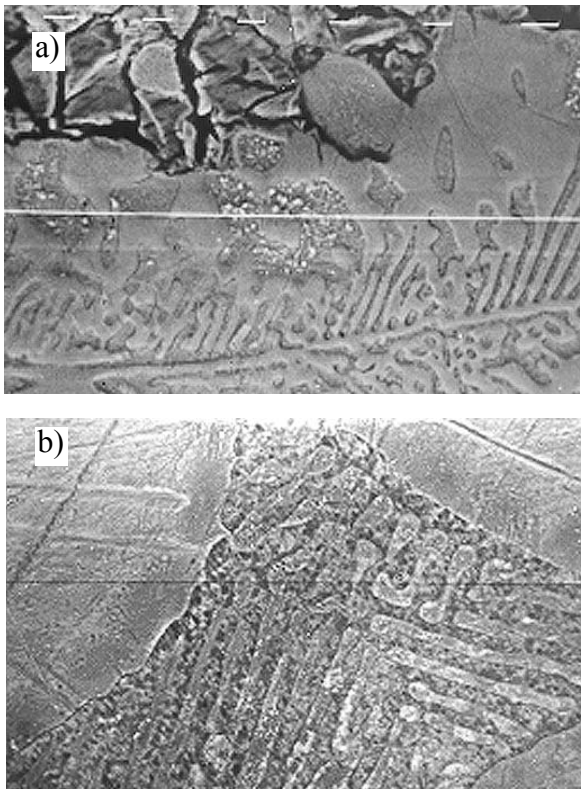


Fig.4. The results of light optic microscopy for the samples with (a) 10wt%Ag (section In:Sb = 1:1) and (b) 40 wt%Ag (section In:Sb = 9:1) Magnification: x150 (a); x300 (b)

performed with standard apparatus used for Vickers hardness measurements. The results, gathered in Table 4, are shown in Fig.7 for the section with In:Sb molar ratio equal to 1:1. Most probably, the increasing amount of HCP_A3 phase influence the increase of the hardness of the alloys. Also, the presence of the intermetallic phases may either decrease ($AgIn_2$) or increase (Ag_2In) the hardness of the alloy.



4. Conclusions

This paper deals with the investigations of the phase relations near ternary eutectic point in the Ag-In-Sb system, which can be a potential lead-free solder.

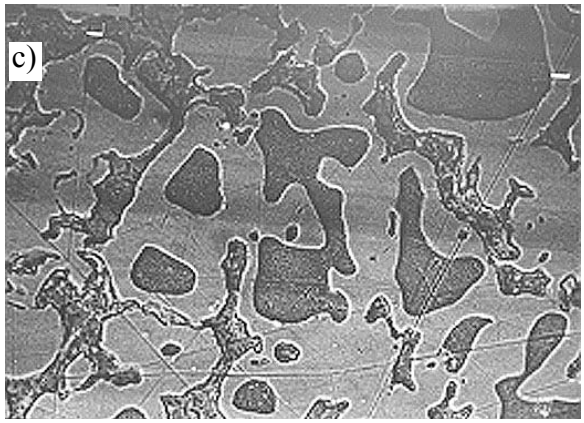


Fig.5. The results of scanning electron microscopy for the samples with: (a) 10wt%Ag (section In:Sb = 1:1), (b) 50wt%Ag (section In:Sb = 7:3) and (c) 40wt%Ag (section In:Sb = 9:1) Magnification: x2000 (a); x3500 (b); x1000 (c)

Table 3. The results of X-ray diffraction analysis for the samples with 10wt%Ag (section In:Sb = 1:1), 50wt%Ag (section In:Sb = 7:3) and 40wt%aAg (section In:Sb = 9:1)

a)

10%wtAg (In:Sb=1:1)	
(nm)	
0.3253	
0.3116	In-Sb
0.2586	Ag-In, Ag-Sb
0.2404	Ag-In, Ag-Sb
0.2277	Ag-In, Ag-Sb
0.2146	In-Sb
0.1869	In-Sb
0.1762	Ag-In, Ag-Sb
0.1490	Ag-In, Ag-Sb
0.1409	In-Sb
0.1362	Ag-In, Ag-Sb

b)

50wt%Ag (In:Sb=7:3)	
(nm)	
0.3769	
0.3563	
0.3112	In-Sb
0.2712	
0.2598	Ag-Sb
0.2402	Ag-In, Ag-Sb
0.2283	Ag-Sb
0.2147	In-Sb
0.1762	Ag-In, Ag-Sb
0.1654	
0.1496	Ag-Sb
0.1411	In-Sb
0.1363	Ag-In, Ag-Sb

c)

40%Ag (In:Sb=9:1)	
(nm)	
0.3762	
0.3568	Ag-In
0.3130	(In)
0.2708	
0.2603	Ag-In
0.2343	Ag-In
0.2239	(In)
0.2156	
0.1655	Ag-In
0.1412	Ag-In
0.1353	(In)

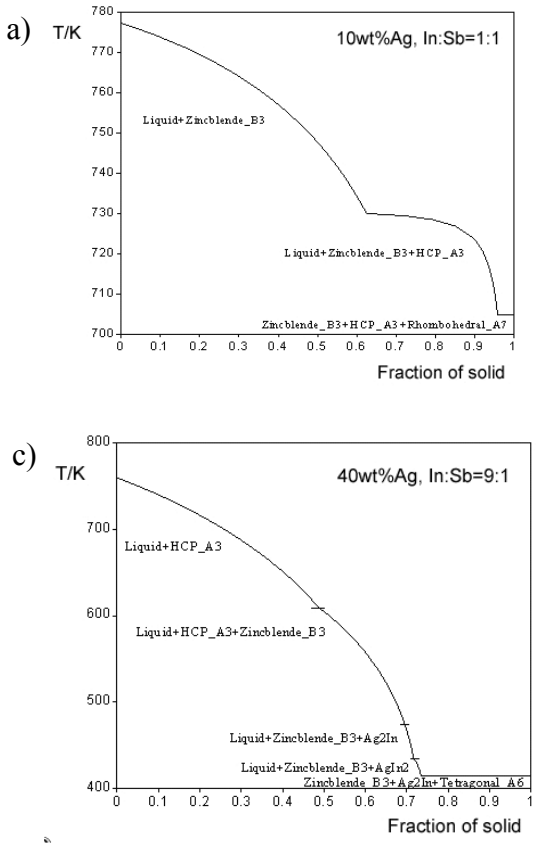


Fig.6. The obtained results for three calculated solidification paths of chosen alloys: (a) equilibrium -scheil model; (b) - scheil model; (c) - scheil model

In the frame of experimental determination, DTA, LOM, SEM and hardness measurement were performed. Based on these results and the results of calculations, phase equilibrium for the isopleths with molar ration of In:Sb = 7:3;

Table 4. The results of hardness measurements

Alloy	Results of measurments	H_V average
10wt%Ag (molar ratio In:Sb=1:1)	101, 102, 103	102
20wt%Ag (molar ratio In:Sb=1:1)	117, 118, 119	118
40wt%Ag (molar ratio In:Sb=1:1)	133, 140	137
50wt%Ag (molar ratio In:Sb=7:3)	109, 109, 110	109
40wt%Ag (molar ratio In:Sb=9:1)	165, 145	155

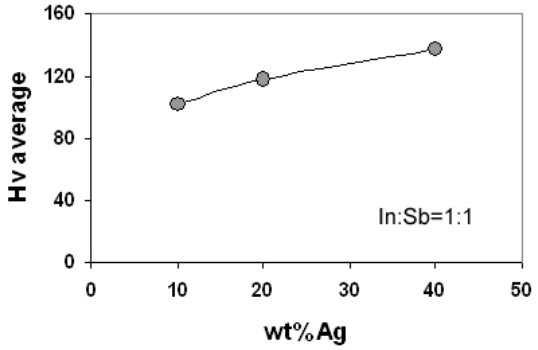


Fig.7. Dependence of hardness on composition for the alloys in section with molar ratio In:Sb=1:1

9:1 and 1:1 was determined. The calculated ternary eutectic point was obtained at temperature of 414,9K and its composition is equal to X_{Ag} = 0,014 and X_{Sb} =0,017. The ternary eutectic is formed during the reaction, which taken place when three tie triangles: (tetragonal A6-L-$AgIn_2$) , ($AgIn_2$-L-Zincblende B3) and (Zincblende B3-L tetragonal A6) descending from higher temperature meet at four-phase plane at eutectic temperature. Then, only one tie-triangle (tetragonal A6-Ag_2In-Zincblende B3) is descending from the four phase plane to lower temperature. The respected solidification path's for three ternary alloys located on three different investigated isopleths are also shown.

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