

EXPERIMENTAL AND THERMODYNAMIC DESCRIPTION OF TERNARY Bi-Cu-Ga SYSTEM

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Abstract

Phase diagram of the Bi-Cu-Ga ternary system has been investigated experimentally with 27 alloys and analytically by using a Calphad method. Thirteen annealed alloys at 200 °C were investigated by using scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS), and X-ray powder diffraction (XRD) methods. Temperatures of phase transformation were determined with 14 alloys which are lying along three vertical sections Bi-Cu0.5Ga0.5, Cu-Bi0.5Ga0.5 and Ga-Bi0.5Cu0.5 by using differential thermal analysis (DTA). Based on the experimental result and by using Calphad method, ternary phase diagrams were constructed with a new description of liquidus phase. Calculated phase diagram and experimentally obtained results are in good agreement. Liquidus projection and invariant reaction were calculated by using new thermodynamic parameters for liquidus phase.

Keywords: Ternary Bi-Cu-Ga system; Calphad method; Experimental results; Liquidus projection.

1. Introduction

Description of phase diagrams is an important task for all researchers over the world. A good way to present phase diagram is by combination experimental results and Calphad method [1, 2]. As a result of combining, these two methods will be a reliable description of total Gibbs energies of phases. By using software such as OpenCalphad [3], ThermoCalc [4], Pandat [5] and many other for visualization of the phase diagram will result in a faster and easier work for industry in their way of searching for best practically applicable alloys. According to this knowledge that Cu and Cu-based alloys have a wide variety of application in a different discipline, investigations of Cu alloys is necessary. The largest user of copper is building industry (roofing, cladding, heating and rainwater system, water pipes, oil and gas lines, electrical wiring, etc.), electronic industry, transportation and many others. Such wide applications of copper is due to the reason that copper is tough, ductile and malleable materials and key properties of copper alloys are excellent

electrical and heat conductivity, good erosion, corrosion and biofouling resistance, high strength, good machinability, non-magnetic, etc. [6-11]. It is important that all used copper is recyclable without any loss of quality. Also copper can easily make alloys with a lot of elements [12-15]. The most important copper alloys are divided into four families, pure coppers, high copper alloys, brass, and bronzes. Chosen ternary system belongs to the brasses family of cast copper-bismuth alloys. To the best of our knowledge, the thermodynamic description of ternary Bi-Cu-Ga system has not been investigated up to now.

2. Experimental procedure

All samples with total masses of about 3 g were prepared from high purity Bi, Cu and Ga (99.999 at. %) produced by Alfa Aesar (Germany) in an induction furnace under high-purity argon atmosphere. The average weight loss of the samples during melting was about 1 mass %.

After melting, samples for the SEM-EDS and XRD investigation were put into quartz glass

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ampoules, sealed under vacuum and annealed at 200 °C for three weeks and quenched into ice water in order to preserve the equilibrium compositions at designated temperature. The average weight loss of the samples during annealing was less than 0.5 mass %.

The compositions of samples and coexisting phases were determined using JEOL JSM-6460 scanning electron microscope with energy dispersive spectroscopy (EDS) (Oxford Instruments X-act).

Powder XRD data for phase identification of samples were recorded on a D2 PHASER (Bruker, Karlsruhe, Germany) powder diffractometer equipped with a dynamic scintillation detector and ceramic X-ray Cu tube (KFL-Cu-2K) in a 2θ range from 10° to 75° with a step size of 0.02° . The patterns were analyzed using the Topas 4.2 software, ICDD databases PDF2 (2013).

Phase transition temperatures were determined by DTA method. The DTA measurements were performed on a DTG-60H (Shimadzu). Alumina crucibles were used and measurements were performed under flowing argon atmosphere. Samples weighing between 20 and 30 mg were investigated at a heating rate of $5^\circ\text{C}/\text{min}$ with three cycles of heating and cooling. The sample masses and heating rates were determined by analysis of one sample at different testing conditions. The reference material was empty alumina crucible. The overall uncertainty of the determined phase transformation temperatures was estimated to be $\pm 1^\circ\text{C}$.

3. Literature data

3.1. The ternary Bi-Cu-Ga system

Up to now in the literature there, exists one paper [16] related to ternary Bi-Cu-Ga system. Gurešić et al. [16] investigated the effect of chemical composition on the microstructure, hardness and electrical conductivity profiles of the Bi-Cu-Ga alloys at 100°C . Properties and phase relation are investigated on 27 ternary alloys. Alloys are experimentally examined with different techniques such as SEM-EDS, XRD, LOM, hardness by Brinell and Vickers and electrical conductivity. In the paper is presented calculated isothermal section at 100°C , which is calculated by using data for constitutive binary systems from literature [17-19]. As the experimental data obtained by EDS are in agreement with calculated phase diagram, the solubility of third element into the binary intermetallic compound is neglected and no ternary compound is found. The crystal structure data for the solid phases in the ternary system are listed in Table 1.

3.2. The binary systems

The three binary systems which are constitutive

systems of this ternary Bi-Cu-Ga system are investigated extensively by a lot of groups. In this work, the thermodynamic parameter for the binary systems are taken from literature [17-19]. Calculated phase diagram Bi-Ga [17], Bi-Cu [18] and Cu-Ga [19] are presented in Figure 1.

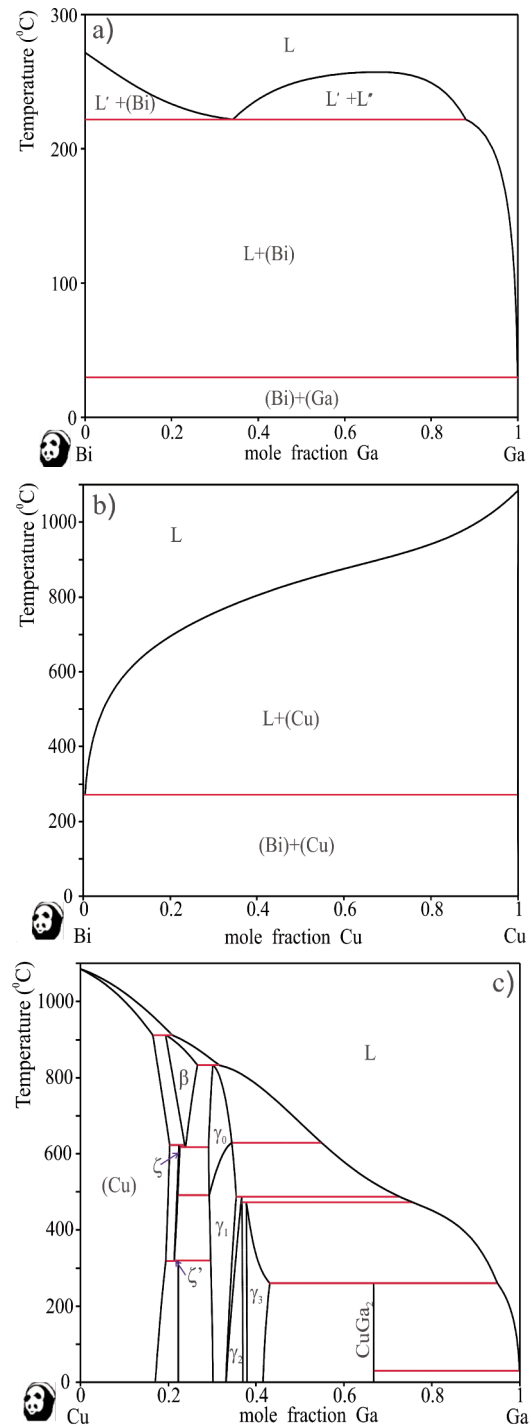


Figure 1. Calculated binary phase diagram a) Bi-Ga [17], b) Bi-Cu [18] and c) Cu-Ga [19].



Table 1. Crystal structure data for the solid phases in the Bi-Cu-Ga system.

Phase	Temperature °C	Composition range	Space grupe	Pearson's symbol	Lattice parameters /nm	Ref.
(Cu)	<1084	83.9-100 at.% Cu (at 25 ^o)	Fm $\bar{3}m$	cF4	$a=b=c=3.6573$	[20]
(Bi)	<271.4	100 at.% Bi (at 25 ^o)	$R\bar{3}m$	$hR2$	$a=b=4.5461$ $c=11.8615$	[21]
(Ga)	<29.7	100 at.% Ga (at 25 ^o)	$Cmca$	$oC8$	$a=4.5197$ $b=7.6633$ $c=4.5260$	[22]
β	616.8-910.9	$Cu_{1-x}Ga_x$ $x=23.9$ at.% Ga (at 616.8 ^o)	$Im\bar{3}m$	cI2	...	[19]
ζ	317.5-622.3	$Cu_{1-x}Ga_x$ $x=21.2$ at.% Ga (at 616.8 ^o)	$P6_3/mmc$	hP2	$a=b=2.60050$ $c=4.25940$	[23]
ζ'	25-319.16	$Cu_{1-x}Ga_x$ $x=22.2$ at.% Ga (at 25 ^o)	$Fm\bar{3}m$...	$a=b=c=3.660$	[24]
γ_0	490.5-832.3	$Cu_{1-x}Ga_x$ $x=29.3$ at.% Ga (at 490.5 ^o)	$P\bar{4}3m$	cP52	$a=b=c=8.71$	[24]
γ_1	25-627.9	$Cu_{1-x}Ga_x$ $x=30-33$ at.% Ga (at 25 ^o)	$P\bar{4}3m$	cP52	$a=b=c=8.747$	[25]
γ_2	25-486.4	$Cu_{1-x}Ga_x$ $x=33.1-37$ at.% Ga (at 25 ^o)	$P\bar{4}3m$	cP52	$a=b=c=8.7186$	[26]
γ_3	25-471.8	$Cu_{1-x}Ga_x$ $x=38-41.5$ at.% Ga (at 25 ^o)	$P\bar{4}3m$	cP52	$a=b=c=8.6954$	[26]
$CuGa_2$	25-259.5	$Cu_{1-x}Ga_x$ $x=66.7$ at.% Ga	$P4/mmm$	tP3	$a=b=2.830$ $c=5.839$	[27]

Binary Bi-Ga is a monotectic system, while Bi-Cu system is simple eutectic system and both are consists of two solid solutions and liquid phase. On binary Bi-Ga at a temperature above 221°C at Gallium rich part liquid phase shows miscibility of the gap. Binary Cu-Ga is more complicated in comparison with other two binary systems. In this system, 11 different phases appear.

4. Experimental results

4.1. Isothermal section at 200 °C

Phase equilibrium at 200 °C has been investigated

with 13 ternary alloys by using SEM-EDS and XRD method. The composition of the samples is checked by mapping entire polished surface of the samples. In Table 2 are given results of the composition of samples and phases determined by the SEM-EDS method. Results of XRD analysis are also given in Table 2 together with calculated lattice parameters. Lattice parameters are determined by using full Rietveld refinement and Topas software. The phases determined with these two methods are in agreement with each other. The same phases detected with SEM-EDS are confirmed with XRD.



Table 2. Experimental results of phase equilibrium in the ternary Bi-Cu-Ga system at 200 °C.

N	Composition at. %	Determined phases		Compositions of phases (at. %)			Lattice parameters (Å)	
		EDS	XRD	Bi	Cu	Ga	<i>a=b</i>	<i>c</i>
1	40.01 Bi	(Cu)	(Cu)	0.60±0.1	82.57±0.2	16.83±0.1	3.6583	3.6583
	47.47 Cu	(Bi)	(Bi)	98.01±0.5	1.19±0.2	0.80±0.2	4.5498	11.8624
	12.52 Ga	ζ'	ζ'	1.03±0.2	77.92±0.6	21.05±0.8	3.6587	3.6587
2	39.89 Bi	(Bi)	(Bi)	98.31±0.3	0.67±0.4	1.02±0.1	4.5411	11.8689
	40.50 Cu	γ ₁	γ ₁	0.32±0.2	67.6±0.3	32.08±0.2	8.7498	8.7498
	19.61 Ga							
3	40.32 Bi	(Bi)	(Bi)	98.32±0.8	1.53±0.1	0.15±0.2	4.5417	11.8676
	29.04 Cu	γ ₃	γ ₃	0.75±0.1	56.52±0.2	42.73±0.3	8.6867	8.6867
	30.64 Ga	CuGa ₂	CuGa ₂	1.62±0.3	35.2±0.5	63.18±0.3	2.8252	5.8313
4	40.04 Bi	L	L	0.61±0.2	9.08±0.4	90.31±0.1	-	-
	15.09 Cu	(Bi)	(Bi)	98.12±0.3	0.86±0.2	1.02±0.1	4.5417	11.8698
	44.87 Ga	CuGa ₂	CuGa ₂	1.72±0.3	32.25±0.4	66.03±0.7	2.8278	5.8382
5	4.58 Bi	(Bi)	(Bi)	98.41±0.1	0.77±0.1	0.82±0.3	4.5476	11.8621
	90.34 Cu	(Cu)	(Cu)	0.33±0.1	94.04±0.1	5.63±0.4	3.6306	3.6306
	5.08 Ga							
6	6.49 Bi	(Bi)	(Bi)	98.71±0.3	0.35±0.8	0.94±0.1	4.5462	11.8692
	81.40 Cu	(Cu)	(Cu)	1.05±0.4	85.77±0.4	13.18±0.1	3.6423	3.6423
	12.11 Ga							
7	12.98 Bi	(Bi)	(Bi)	97.8±0.7	1.12±0.3	1.08±0.3	4.5487	11.8619
	64.41 Cu	ζ'	ζ'	1.35±0.5	75.92±0.6	22.73±0.2	3.6612	3.6612
	22.61 Ga	γ ₁	γ ₁	0.91±0.4	68.78±0.2	30.31±0.5	8.7501	
8	15.61 Bi	(Bi)	(Bi)	98.37±0.4	0.51±0.2	1.12±0.4	4.5417	11.8598
	33.89 Cu	γ ₃	γ ₃	2.63±0.2	55.87±0.3	41.5±0.3	8.6893	8.6893
	50.5 Ga	CuGa ₂	CuGa ₂	0.17±0.1	33.8±0.3	66.03±0.1	2.829	5.8372
9	8.99 Bi	L	L	4.93±0.1	2.37±0.2	92.7±0.5	-	-
	10.84 Cu	(Bi)	(Bi)	98.91±0.2	0.58±0.1	0.51±0.3	4.5478	11.8608
	80.17 Ga	CuGa ₂	CuGa ₂	0.35±0.2	32.02±0.5	67.63±0.7	2.8301	5.8392
10	15.30 Bi	L	L	6.52±0.6	2.37±0.5	91.11±0.1	-	-
	22.18 Cu	(Bi)	(Bi)	98.13±0.4	0.56±0.3	1.31±0.1	4.5498	11.8627
	62.52 Ga	CuGa ₂	CuGa ₂	2.45±0.6	32.74±0.4	64.81±0.2	2.8245	5.8307
11	20.91 Bi	(Bi)	(Bi)	98.1±0.2	0.77±0.4	1.13±0.4	4.5401	11.8621
	37.97 Cu	γ ₃	γ ₃	1.35±0.1	58.24±0.5	40.41±0.3	8.6913	8.6913
	41.12 Ga	CuGa ₂	CuGa ₂	1.32±0.1	33.88±0.1	64.80±0.2	2.8298	5.8376
12	32.97 Bi	(Bi)	(Bi)	97.31±0.3	0.88±0.1	1.81±0.1	4.5413	11.8642
	40.73 Cu	γ ₃	γ ₃	1.78±0.6	60.11±0.2	38.11±0.2	8.6928	8.6928
	26.30 Ga							
13	26.95 Bi	(Bi)	(Bi)	97.5±0.3	0.47±0.3	2.03±0.2	4.5434	11.8615
	66.73 Cu	(Cu)	(Cu)	1.35±0.2	88.15±0.2	10.5±0.2	3.6401	3.6401
	6.32 Ga							

Results presented in Table 2, confirmed the existence of seven different phase regions. Samples marked with numbers 5, 6, and 13 determined same two-phase regions, (Cu)+(Bi). In the equilibrium of samples 3, 8, and 11, the same three-phase regions were determined, (Bi)+ γ_3 +CuGa₂. Samples 4, 9, and 10 are from three-phase region L+(Bi)+CuGa₂. In microstructures of the samples, 1 and 7 are two different three-phase regions (Cu)+(Bi)+ ζ' and (Bi)+ ζ' + γ_{11} , respectively. Samples 2 and 12 are confirmed to be in two different two-phases regions (Bi)+ γ_1 and (Bi)+ γ_3 , respectively. EDS results of four detected binary intermetallics compound (ζ' , γ_1 , γ_3 , and CuGa₂) show small solubility of the third element. Solubility in most cases is smaller than 2 at. % except for samples 8 and 10. Intermetallic compound γ_3 detected in sample 3 dissolves 2.63±0.2 at.% of Bi and intermetallic compound CuGa₂ detected in sample 10 dissolves 2.45±0.6 at.% of Bi. The detected solubility of Ga and Cu into solid solution (Bi) is small for most samples,

except for sample 13, where the amount of Ga reaches 2.03±0.2 at. %. Solid solution (Cu) dissolves a small amount of Bi and a significant amount of Ga, but according to the study of the binary systems, this was expected. The maximum solubility of Ga into (Cu) solid solution at 200 °C temperature is ≈18 at.% of Ga.

In Figure 2 are given eight BEC micrographs of samples with marked phases.

4.2. Vertical sections

Phase transition temperatures of the 14 selected samples along three vertical sections were experimentally determined using DTA method. Solid stable transition temperatures were determined from the onset of the corresponding peak. The liquid temperatures were evaluated from the peak maximum. Obtained DTA data are given in Table 3. Temperatures presented in Table 3 are taken from the first heating cycle.

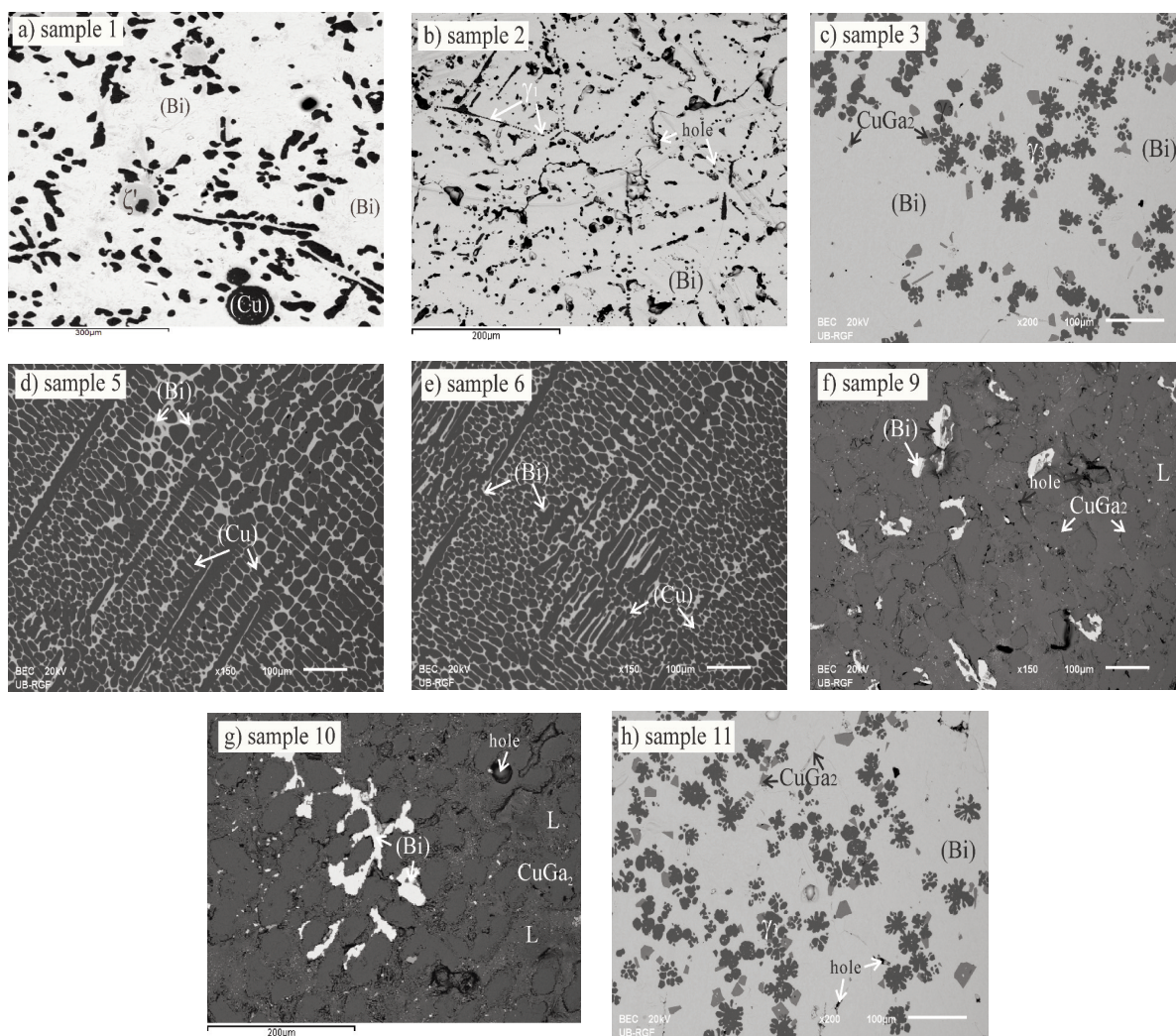


Figure 2. SEM micrographs of the selected alloy samples annealed at 200 °C for four weeks.

Table 3. Phase transition temperatures along three vertical sections in the ternary Bi-Cu-Ga system.

Nominal composition (at.%)	Phase transition temperatures (°C)			
	Other peak			Liquid
Vertical section Bi–Cu ₅₀ Ga ₅₀				
Bi ₂₀ Cu ₄₀ Ga ₄₀	217.5	627.4		771.5
Bi ₄₀ Cu ₃₀ Ga ₃₀	215.7			910.1
Bi ₆₀ Cu ₂₀ Ga ₂₀	221.8	253.5		920.6
Bi ₈₀ Cu ₁₀ Ga ₁₀	223.8	250.9		803.3
Bi ₉₅ Cu _{2.5} Ga _{2.5}	221.5	250.3		591.1
Vertical section Cu–Bi ₅₀ Ga ₅₀				
Bi ₄₀ Cu ₂₀ Ga ₄₀	230.1	244.2	627.3	740.5
Bi ₃₀ Cu ₄₀ Ga ₃₀	227.5	630.4		922.1
Bi ₂₀ Cu ₆₀ Ga ₂₀	271.5	320.8	492.4	622.4
Bi ₁₀ Cu ₈₀ Ga ₁₀	273.7			934.3
Vertical section Ga–Bi ₅₀ Cu ₅₀				
Bi ₄₀ Cu ₄₀ Ga ₂₀	265.8	780.4		1025.3
Bi ₃₀ Cu ₃₀ Ga ₄₀	228.2	249.1	630.5	824.3
Bi ₂₀ Cu ₂₀ Ga ₆₀	29.7	223.7	243.7	519.3
Bi ₁₀ Cu ₁₀ Ga ₈₀	30.1	229.5	243.1	354.8
Bi _{2.5} Cu _{2.5} Ga ₉₅	31.5			190.5

5. Thermodynamic modeling

The Bi-Cu-Ga ternary system was thermodynamically assessed by CALPHAD method [1, 2] using Thermo-calc software package [4]. Thermodynamic parameters for constitutive binary systems were taken from literature [17-19].

After a critical evaluation of experimental results and literature data in this work, the Liquid phase is thermodynamically assessed and, all other phases are treated as pure binary phases. The detected solubility of the third element in γ_3 (sample 3) and CuGa₂ (sample 10) is not considered in the modeling because this was considered as an error due to the fact that other results of this compound detected small solubility of the third element. Also, the solubility of Ga (sample 13) into solid solution (Bi) is not used in the modeling because this large amount is detected just in one sample.

5.1. Unary phase

The thermodynamic parameters for Bi, Cu, and Ga were taken from the literature published by Dinsdale [28], which are described by Eq. 1.

$$G_i(T) - H_i^{SER} = A + B \cdot T + C \cdot T \ln T + D \cdot T^2 + E \cdot T^{-1} + F \cdot T^3 + I \cdot T^7 + J \cdot T^{-9} \quad (1)$$

where H_i^{SER} is the molar enthalpy of the elements i at 298.15 K and 1 bar in standard element reference (SER) state, T is absolute temperature.

5.2. Solution phases

The ternary solution phases (ϕ =liquid) is treated as a substitutional solution. The Gibbs free energy is expressed by Redlich-Kister polynomial [29]:

$$G_m^\phi = x_{Bi} G_{Bi}^\phi + x_{Cu} G_{Cu}^\phi + x_{Ga} G_{Ga}^\phi + RT(x_{Bi} \ln x_{Bi} + x_{Cu} \ln x_{Cu} + x_{Ga} \ln x_{Ga}) + x_{Bi} x_{Cu} L_{Bi,Cu}^\phi + x_{Bi} x_{Ga} L_{Bi,Ga}^\phi + x_{Cu} x_{Ga} L_{Cu,Ga}^\phi + {}^{ex} G_{Bi,Cu,Ga}^\phi \quad (2)$$

where x_{Bi} , x_{Cu} and x_{Ga} are molar fractions of elements Bi, Cu, and Ga, respectively.

G_{Bi}^ϕ , G_{Cu}^ϕ and G_{Ga}^ϕ are the Gibbs energies of Bi, Cu, and Ga in ϕ phase. R is gas constant, T temperature, and $RT(x_{Bi} \ln x_{Bi} + x_{Cu} \ln x_{Cu} + x_{Ga} \ln x_{Ga})$ corresponds to the contribution of the ideal entropy of mixing to the Gibbs energy. $L_{Bi,Cu}^\phi$, $L_{Bi,Ga}^\phi$ and $L_{Cu,Ga}^\phi$ are interaction parameters from the corresponding binary systems [17-19]. The ${}^{ex} G_{Bi,Cu,Ga}^\phi$ term in Eq. 2 is the ternary excess Gibbs energy, which is expressed as:

$${}^{ex} G_{Bi,Cu,Ga}^\phi = x_{Bi} x_{Cu} x_{Ga} \left(x_{Bi}^0 L_{Bi,Cu,Ga}^\phi + x_{Cu}^1 L_{Bi,Cu,Ga}^\phi + x_{Ga}^2 L_{Bi,Cu,Ga}^\phi \right) \quad (3)$$

where ${}^0 L_{Bi,Cu,Ga}^\phi$, ${}^1 L_{Bi,Cu,Ga}^\phi$ and ${}^2 L_{Bi,Cu,Ga}^\phi$ are ternary interaction parameters which are described by using Kaptay equation [30, 31]:

$${}^i L_{Bi,Cu,Ga}^\phi = h_i \cdot \exp(-T / \tau_i) \quad (4)$$

where h_i is the enthalpy part of interaction energy and τ_i is a special temperature.

6. Thermodynamic modeling and calculations

Based on literature data and present experimental data, the thermodynamic optimization of Bi-Cu-Ga system has been performed. The optimization of the parameters was conducted using the PARROT module based on a least square procedure. The thermodynamic parameters for liquid phase obtained in this work and literature parameters taken from the literature are present in Table 4 in the unit of J/mol of the atom.

All of the binary compounds are treated as pure binary ones since the solid solubility for the third element in most cases is negligible. In Figure 3 is presented calculated isothermal section at 100 °C compared with experimental data from literature [16]. Figure 4 presents a comparison between the calculated and the experimental phase relations at 200 °C from this work.



Table 4. The thermodynamic parameters for the ternary Bi-Cu-Ga system.

Phase, name in database and model	Thermodynamic parameters	References
L LIQUID (Bi, Cu, Ga)	${}^0L_{Bi,Ga}^{Liquid} = 8401.6 + 0.996135 \cdot T$	[17]
	${}^1L_{Bi,Ga}^{Liquid} = -560.9 - 2.43423 \cdot T$	[17]
	${}^2L_{Bi,Ga}^{Liquid} = 754.8 - 0.682275 \cdot T$	[17]
	${}^3L_{Bi,Ga}^{Liquid} = -1162.5$	[17]
	${}^0L_{Bi,Cu}^{Liquid} = 20747.5 - 5.85 \cdot T$	[18]
	${}^1L_{Bi,Cu}^{Liquid} = -4925 + 2.55 \cdot T$	[18]
	${}^2L_{Bi,Cu}^{Liquid} = 4387.5 - 2.3 \cdot T$	[18]
	${}^0L_{Cu,Ga}^{Liquid} = -58110.5 + 154.5439 \cdot T - 18.3753 \cdot T \cdot \ln(T)$	[19]
	${}^1L_{Cu,Ga}^{Liquid} = -33884.7 + 1.9151 \cdot T$	[19]
	${}^2L_{Cu,Ga}^{Liquid} = -11256.9$	[19]
	${}^0L_{Bi,Cu,Ga}^{Liquid} = -5897.57 \cdot \exp(-0.001333 \cdot T)$	This work
	${}^1L_{Bi,Cu,Ga}^L = -21423.7 \cdot \exp(-0.000289 \cdot T)$	This work
${}^2L_{Bi,Cu,Ga}^L = -3977.0$	This work	
(Cu) FCC_A1 (Bi, Cu, Ga) ₁ (Va) ₁	${}^0L_{Cu,Ga:Va}^{FCC_A1} = -38799.9 + 17.8403 \cdot T$	[19]
	${}^1L_{Cu,Ga:Va}^{FCC_A1} = -38704.9 - 16.5753 \cdot T$	[19]
	${}^0L_{Bi,Cu:Va}^{FCC_A1} = 50 \cdot T$	[18]
B BCC_A2 (Cu, Ga) ₁ (Va) ₃	${}^0L_{Cu,Ga:Va}^{BCC_A2} = -55966.9 + 24.5934 \cdot T$	[19]
	${}^1L_{Cu,Ga:Va}^{BCC_A2} = -29932.0 - 28.7715 \cdot T$	[19]
ζ HCP_A3 (Cu, Ga) ₁ (Va) _{0.5}	${}^0L_{Cu,Ga:Va}^{HCP_A3} = -44826.0 + 12.5993 \cdot T$	[19]
	${}^1L_{Cu,Ga:Va}^{HCP_A3} = -36117.4 - 9.0 \cdot T$	[19]
(Ga) ORTHORHOMBIC (Ga) ₁ (Va) ₁	${}^0L_{Ga:Va}^{ORTHORHOMBIC} = G_{Ga}^{SER}$	[19]
ζ CU8GA2_ZETA (Cu) _{0.778} (Ga) _{0.222}	${}^0L_{Cu:Ga}^{CU8GA2_ZETA} = -10100.0 - 4.4596 \cdot T + 0.778 \cdot G_{Cu}^{SER} + 0.222 \cdot G_{Ga}^{SER}$	[19]
CuGa ₂ CUGA2 (Cu) ₁ (Ga) ₂	${}^0L_{Cu:Ga}^{CUGA2} = -23437.9 - 13.2663 \cdot T + G_{Cu}^{SER} + 2 \cdot G_{Ga}^{SER}$	[19]
γ ₀ CU9GA4_GAMMA0 (Cu) ₆ (Cu,Ga) ₆ (Ga) ₁	${}^0L_{Cu:Cu,Ga:Ga}^{CU9GA4_GAMMA0} = -998310.4 + 234.1156 \cdot T$	[19]
	${}^0L_{Cu:Cu:Ga}^{CU9GA4_GAMMA0} = 157967.9 - 99.2709 \cdot T + 12 \cdot G_{Cu}^{SER} + G_{Ga}^{SER} - 1$	[19]
	${}^0L_{Cu:Ga:Ga}^{CU9GA4_GAMMA0} = 27365.9 - 84.6505 \cdot T + 6 \cdot G_{Cu}^{SER} + 7 \cdot G_{Ga}^{SER} - 1$	[19]
γ ₁ CU9GA4_GAMMA1 (Cu) ₆ (Cu,Ga) ₃ (Cu,Ga) ₃ (Ga) ₁	${}^0L_{Cu:Cu:Cu:Ga}^{CU9GA4_GAMMA1} = 157967.9 - 99.2709 \cdot T + 12 \cdot G_{Cu}^{SER} + G_{Ga}^{SER}$	[19]
	${}^0L_{Cu:Ga:Ga:Ga}^{CU9GA4_GAMMA1} = 27365.9 - 84.6505 \cdot T + 6 \cdot G_{Cu}^{SER} + 7 \cdot G_{Ga}^{SER}$	[19]
	${}^0L_{Cu:Cu:Cu:Ga}^{CU9GA4_GAMMA1} = 0.5 \cdot (157967.9 - 99.2709 \cdot T + 12 \cdot G_{Cu}^{SER} + G_{Ga}^{SER}) + 0.5 \cdot (27365.9 - 84.6505 \cdot T + 6 \cdot G_{Cu}^{SER} + 7 \cdot G_{Ga}^{SER}) - 9660.7 - 13.3550 \cdot T - 249577.6 + 58.5289 \cdot T$	[19]

Table 4 is continued on the next page.



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	${}^0L_{Cu:Ga:Cu:Ga}^{CU9GA4_GAMMA1} = 0.5 \cdot (157967.9 - 99.2709 \cdot T + 12 \cdot G_{Cu}^{SER} + G_{Ga}^{SER}) + 0.5 \cdot (27365.9 - 84.6505 \cdot T + 6 \cdot G_{Cu}^{SER} + 7 \cdot G_{Ga}^{SER}) - 9660.7 - 13.3550 \cdot T - 249577.6 + 58.5289 \cdot T$	[19]
	${}^0L_{Cu:Cu:Ga:Cu:Ga}^{CU9GA4_GAMMA1} = -9660.7 - 13.3550 \cdot T + 4714.0 - 249577.6 + 58.5289 \cdot T$	[19]
	${}^1L_{Cu:Cu:Ga:Cu:Ga}^{CU9GA4_GAMMA1} = -4714.0$	[19]
	${}^0L_{Cu:Cu:Cu:Ga:Ga}^{CU9GA4_GAMMA1} = -9660.7 - 13.3550 \cdot T + 4714.0 - 249577.6 + 58.5289 \cdot T$	[19]
	${}^1L_{Cu:Cu:Cu:Ga:Ga}^{CU9GA4_GAMMA1} = -4714.0$	[19]
	${}^0L_{Cu:Cu:Ga:Ga:Ga}^{CU9GA4_GAMMA1} = -9660.7 - 13.3550 \cdot T - 4714.0 - 249577.6 + 58.5289 \cdot T$	[19]
	${}^1L_{Cu:Cu:Ga:Ga:Ga}^{CU9GA4_GAMMA1} = -4714.0$	[19]
	${}^0L_{Cu:Ga:Cu:Ga:Ga}^{CU9GA4_GAMMA1} = -9660.7 - 13.3550 \cdot T - 4714.0 - 249577.6 + 58.5289 \cdot T$	[19]
	${}^1L_{Cu:Ga:Cu:Ga:Ga}^{CU9GA4_GAMMA1} = -4714.0$	[19]
γ_2 $CU9GA4_GAMMA2$ $(Cu)_3(Cu, Va)_3(Cu, Ga)_3(Ga)_4$	${}^0L_{Cu:Cu:Cu:Ga}^{CU9GA4_GAMMA2} = 0.5 \cdot (157967.9 - 99.2709 \cdot T + 12 \cdot G_{Cu}^{SER} + G_{Ga}^{SER}) + 0.5 \cdot (27365.9 - 84.6505 \cdot T + 6 \cdot G_{Cu}^{SER} + 7 \cdot G_{Ga}^{SER}) - 9660.7 - 13.3550 \cdot T - 249577.6 + 58.5289 \cdot T$	[19]
	${}^0L_{Cu:Cu:Ga:Ga}^{CU9GA4_GAMMA2} = 27365.9 - 84.6505 \cdot T + 6 \cdot G_{Cu}^{SER} + 7 \cdot G_{Ga}^{SER}$	[19]
	${}^0L_{Cu:Va:Cu:Cu:Ga}^{CU9GA4_GAMMA2} = 6 \cdot G_{Cu}^{SER} + 4 \cdot G_{Ga}^{SER}$	[19]
	${}^0L_{Cu:Va:Ga:Ga}^{CU9GA4_GAMMA2} = 3 \cdot G_{Cu}^{SER} + 7 \cdot G_{Ga}^{SER}$	[19]
	${}^0L_{Cu:Cu:Va:Cu:Ga}^{CU9GA4_GAMMA2} = -87862.1 - 18.4959 \cdot T$	[19]
	${}^0L_{Cu:Cu:Va:Ga:Ga}^{CU9GA4_GAMMA2} = 0$	[19]
	${}^0L_{Cu:Cu:Cu:Ga:Ga}^{CU9GA4_GAMMA2} = -9660.7 - 13.3550 \cdot T - 4714.0 - 249577.6 + 58.5289 \cdot T$	[19]
	${}^1L_{Cu:Cu:Cu:Ga:Ga}^{CU9GA4_GAMMA2} = -4714.0$	[19]
	${}^0L_{Cu:Va:Cu:Cu:Ga}^{CU9GA4_GAMMA2} = -325261.8 + 205.6819 \cdot T$	[19]
γ_3 $CU9GA4_GAMMA3$ $(Cu, Va)_6(Cu, Ga)_3(Ga)_4$	${}^0L_{Cu:Cu:Cu:Ga}^{CU9GA4_GAMMA3} = 0.5 \cdot (157967.9 - 99.2709 \cdot T + 12 \cdot G_{Cu}^{SER} + G_{Ga}^{SER}) + 0.5 \cdot (27365.9 - 84.6505 \cdot T + 6 \cdot G_{Cu}^{SER} + 7 \cdot G_{Ga}^{SER}) - 9660.7 - 13.3550 \cdot T - 249577.6 + 58.5289 \cdot T$	[19]
	${}^0L_{Cu:Ga:Ga}^{CU9GA4_GAMMA3} = 27365.9 - 84.6505 \cdot T + 6 \cdot G_{Cu}^{SER} + 7 \cdot G_{Ga}^{SER}$	[19]
	${}^0L_{Va:Cu:Cu:Ga}^{CU9GA4_GAMMA3} = 3 \cdot G_{Cu}^{SER} + 4 \cdot G_{Ga}^{SER}$	[19]
	${}^0L_{Va:Ga:Ga}^{CU9GA4_GAMMA3} = 50000 + 7 \cdot G_{Ga}^{SER}$	[19]
	${}^0L_{Cu:Va:Cu:Cu:Ga}^{CU9GA4_GAMMA3} = -48276.5 + 166.7149 \cdot T$	[19]

Table 4 is continued on the next page.



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	${}^0L_{Cu,Va:Ga:Ga}^{CU9GA4_GAMMA3} = 0$	[19]
	${}^0L_{Cu:Cu, Ga: Ga}^{CU9GA4_GAMMA3} = -9660.7 - 13.3550 \cdot T - 4714.0 - 249577.6 + 58.5289 \cdot T$	[19]
	${}^1L_{Cu:Cu, Ga: Ga}^{CU9GA4_GAMMA3} = -4714.0$	[19]
	${}^0L_{Va:Cu, Ga: Ga}^{CU9GA4_GAMMA3} = -238466.3$	[19]
(Bi) RHOMBO_A7 (Bi) ₁	${}^0L_{Bi}^{RHOMBO_A7} = G_{Bi}^{SER}$	[17]

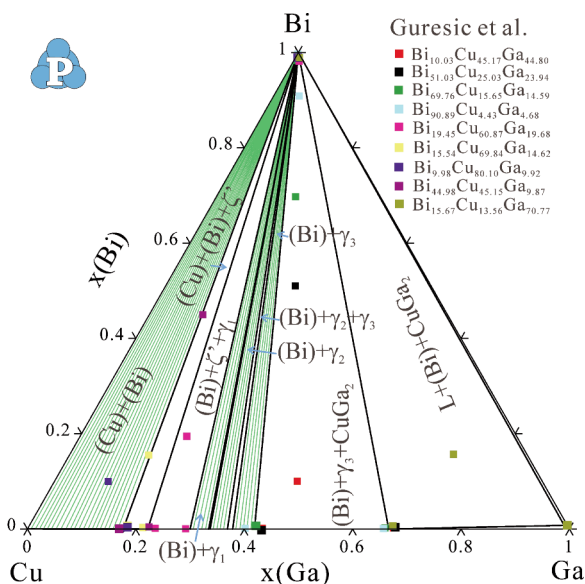


Figure 3. The calculated isothermal section at 100 °C compared with experimental data from literature [16].

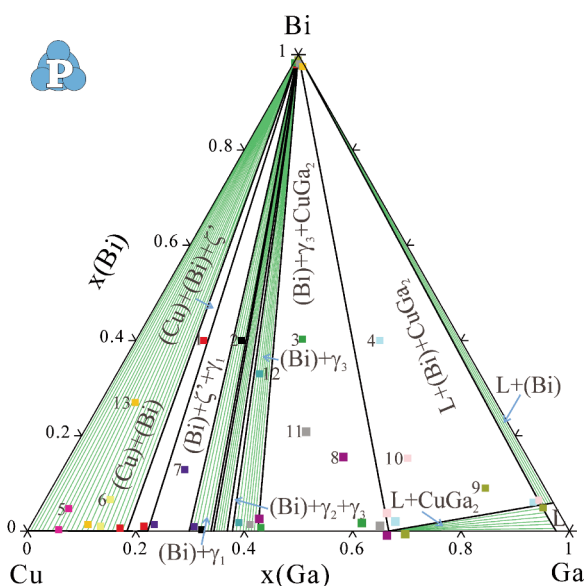


Figure 4. The calculated isothermal section at 200 °C compared with experimental data from this work.

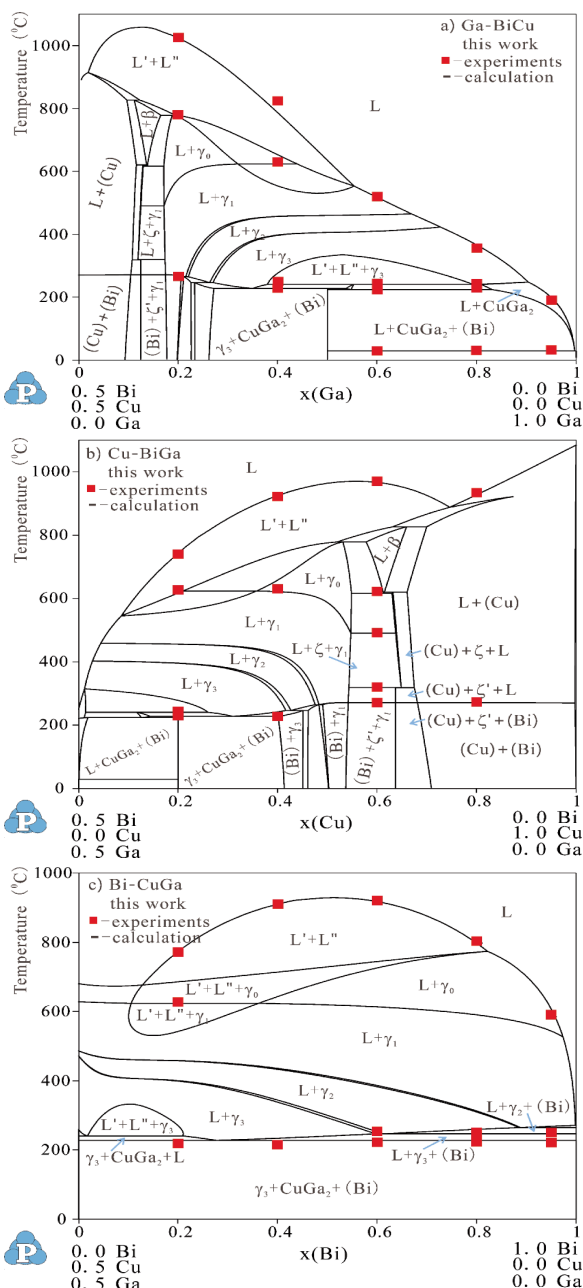


Figure 5. Calculated vertical sections of the Bi-Cu-Ga ternary system compared with the present experimental data: a) Ga-BiCu, b) Cu-BiGa and c) Bi-CuGa.



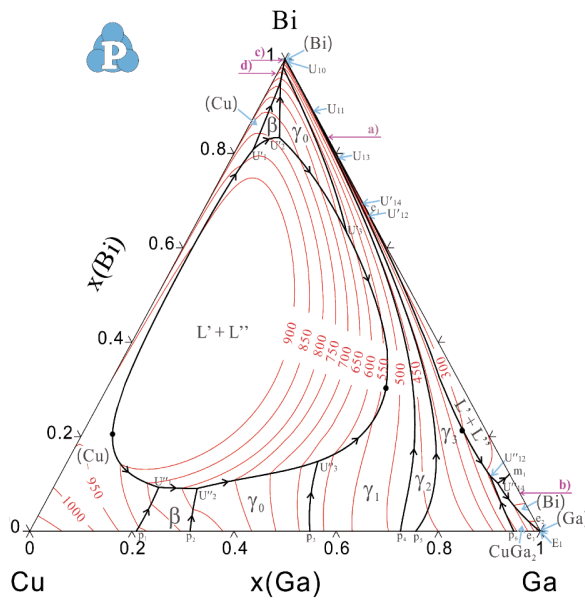


Figure 6. Predicted liquidus projection of the ternary Bi-Cu-Ga system with isotherms line in °C.

In Figure 5 are presented calculated vertical sections compared with experimentally determined temperatures of the phase transformation. As can be seen from Fig. 5, the calculations are in agreement with most of the experimental data.

By using optimized parameters presented in this study liquidus projection was calculated and presented in Fig. 6.

In Figure 7 are given magnified part of liquidus projection. Positions of magnified parts are marked in figure 6.

Furthermore, from the presented liquidus surface projection, the existence of sixteen invariant reactions is suggested. The calculated temperatures of invariant equilibria and the corresponding compositions of liquid phases are listed in Table 5. One reaction is a peritectic type marked with symbol P, and fourteen reactions are univariant type marked with symbol U and the least one is a eutectic type with symbol E.

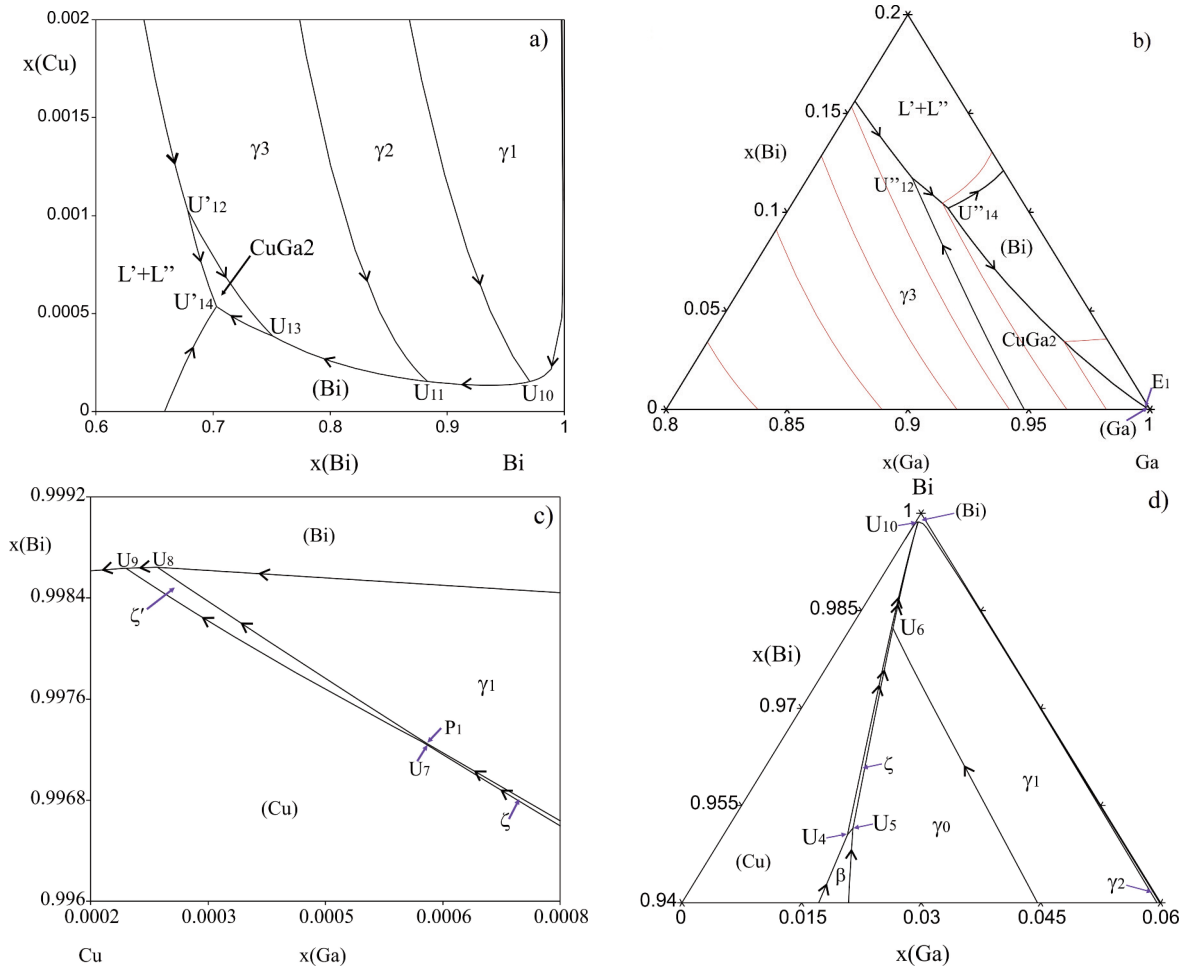


Figure 7. Magnified liquidus projection of the ternary Bi-Cu-Ga system.



Table 5. Predicted invariant reactions involving the liquid phase in the Bi-Cu-Ga ternary system. (U, P and E abbreviation are univariant, peritectic and eutectic respectively).

T (°C)	Invariant reaction	Type	Phase	at.%(Bi)	at.%(Cu)	at.%(Ga)
826.6	$L' + (\text{Cu}) \rightarrow L'' + \beta$	U_1	L'	80.9	15.7	3.4
			(Cu)	0.06	82.29	17.65
			β	-	75.46	24.54
			L''	9.29	70.09	20.62
778.6	$L' + \beta \rightarrow L'' + \gamma^0$	U_2	L'	83.32	9.44	7.24
			β	-	74.18	25.82
			L''	9.04	62.68	28.28
			γ^0	-	70.22	29.78
623.6	$L' + \gamma^0 \rightarrow L'' + \gamma^1$	U_3	L'	63.25	6.32	30.43
			γ^0	-	66.09	33.91
			L''	14.79	36.17	49.04
			γ^1	-	66.08	33.92
620.6	$(\text{Cu}) + \beta \rightarrow L + \zeta$	U_4	(Cu)	0.05	79.61	20.34
			β	-	76.23	23.77
			L	95.04	3.41	1.55
			ζ	-	77.55	22.45
616.9	$L + \beta \rightarrow \zeta + \gamma^0$	U_5	L	95.15	3.28	1.57
			β	-	76.09	23.91
			ζ	-	77.39	22.61
			γ^0	-	70.88	29.12
490.6	$L + \gamma^0 \rightarrow \gamma^1 + \zeta$	U_6	L	98.22	1.25	0.53
			γ^0	-	70.74	29.26
			γ^1	-	70.73	29.27
			ζ	-	77.88	22.12
319.2	$L + \gamma^1 + \zeta \rightarrow \zeta'$	P_1	L	99.72	0.22	0.06
			γ^1	-	70.39	29.61
			ζ	-	78.68	21.32
			ζ'	-	77.8	22.2
318.7	$L + \zeta \rightarrow \zeta' + (\text{Cu})$	U_7	L	99.73	0.21	0.06
			ζ	-	78.69	21.31
			ζ'	-	77.8	22.2
			(Cu)	0.03	80.55	19.42
271.1	$L + \gamma^1 \rightarrow (\text{Bi}) + \zeta'$	U_8	L	99.86	0.11	0.03
			γ^1	-	70.28	29.72
			(Bi)	100	-	-
			ζ'	-	77.8	22.2
271.1	$L + \zeta' \rightarrow (\text{Bi}) + (\text{Cu})$	U_9	L	99.86	0.11	0.03
			ζ'	-	77.8	22.2
			(Bi)	100	-	-
			(Cu)	0.02	81.01	18.97

Table 5 is continued on the next page.



Table 5 continues from the previous page

264.9	$L + \gamma^1 \rightarrow \gamma^{2+} + (\text{Bi})$	U_{10}	L	97.04	0.02	2.94
			γ^1	-	65.82	34.18
			γ^2	-	65.13	34.87
			(Bi)	100	-	-
246.5	$L + \gamma^2 \rightarrow (\text{Bi}) + \gamma^3$	U_{11}	L	88.32	0.01	11.67
			γ^2	-	63.15	36.85
			(Bi)	100	-	-
			γ^3	-	62.18	37.82
240.6	$L' + \gamma^3 \rightarrow L'' + \text{CuGa}_2$	U_{12}	γ^3	-	57.14	42.86
			L'	67.8	0.11	32.09
			L''	11.71	3.98	84.31
			CuGa_2	-	33.3	66.7
227.7	$L + \gamma^3 \rightarrow (\text{Bi}) + \text{CuGa}_2$	U_{13}	L	75.08	0.04	24.88
			γ^3	-	57.25	42.75
			(Bi)	100	-	-
			CuGa_2	-	33.3	66.7
224.1	$L' + \text{CuGa}_2 \rightarrow L'' + (\text{Bi})$	U_{14}	L'	70.27	0.05	29.68
			CuGa_2	-	33.3	66.7
			L''	10.18	3.26	86.56
			(Bi)	100	-	-
29.4	$L \rightarrow \text{CuGa}_2 + (\text{Bi}) + (\text{Ga})$	E_1	L	0.13	0.14	99.73
			CuGa_2	-	33.3	66.7
			(Bi)	100	-	-
			(Ga)	-	-	100

7. Conclusions

The ternary Bi-Cu-Ga system was experimentally investigated using DTA, SEM-EDS and XRD methods and assessed using the CALPHAD approach. Phase transformation temperatures were detected by using DTA measurement on 14 alloy samples from three vertical sections.

The isothermal section at 200 °C was investigated with 13 ternary alloys with SEM-EDS and XRD methods. Seven different phase region were detected with SEM-EDS and XRD method. The calculated isothermal section at 200 °C shows thirteen phase region from which seven are experimentally confirmed.

Based on present experimental data and literature data, a thermodynamic modeling of the Bi-Cu-Ga system was performed. Generally, a satisfactory agreement between calculated results and experimental data is reached. Liquidus surface projection of the ternary Bi-Cu-Ga system was calculated in which these are sixteen invariant reactions.

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