THERMODYNAMIC ASSESSMENT OF THE BA-CU-Y TERNARY SYSTEM. DIRECT OPTIMIZATION OF THE MISCIBILITY GAP

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ABSTRACT Processing the experimental tie-lines in the miscibility gap of the Ba-Cu-Y ternary liquid alloys coupled with the Gibbs energies of the Ba-Cu and Cu-Y binaries estimated earlier has led to description of the Gibbs energy of the ternary melt and to the complete ternary phase diagram. The transformation of an open triangular simplex to the plane that can ease significantly optimization and calculation of the ternary phase diagrams is suggested. The literature and present results are discussed.

1. Introduction

The present work is a part of the project [1] devoted to the complete assessment of the famous Y-Ba-Cu-O phase diagram containing the oxide high temperature superconductor phases. The thermodynamics of the phases in the Ba-Cu-Y system are necessary for thermodynamic modeling of the quaternary system, and besides, the complete phase diagram of the Ba-Cu-Y system may be interesting to find a metallic precursor for producing the superconductors (see Ref. [2] for discussion).

The optimization of the Ba-Cu and Cu-Y binary phase diagrams was made by us earlier [3, 4]. There is no any experimental values for the Ba-Y phase diagram. According to Refs. [5, 6] the latter should have a miscibility gap with the upper critical point in the liquid phase and negligible primary solid solutions. This is confirmed by the experimental study of the isothermal cross section of the Ba-Cu-Y system at 1273 K [7] where the coordinates of the tie-lines in the ternary miscibility gap have been measured.

In the present work, the experimental values for the Ba-Cu-Y ternary system [7] and thermodynamic properties of the phases in the Ba-Cu and Cu-Y binaries [3, 4] have been employed to describe the Ba-Cu-Y ternary system and the Ba-Y binary.

2. Direct optimization of the miscibility gap in the Ba-Cu-Y liquid alloys

The polynomial model as follows has been used to present the Gibbs energy of the Ba-Cu-Y liquid alloys

$$\Delta_{\text{mix}}G(T, x_{Cu}, x_Y) = x_{Ba} RT \ln x_{Ba} + x_{Cu} RT \ln x_{Cu} + x_Y RT \ln x_Y +$$
$$+ x_{Ba}x_{Cu} \sum_k (A_k^{BaCu} + TB_k^{BaCu} + TC_k^{BaCu} \ln T)(x_{Cu} - x_{Ba})^k +$$
$$+ x_{Cu}x_Y \sum_l (A_l^{CuY} + TB_l^{CuY} + TC_l^{CuY} \ln T)(x_Y - x_{Cu})^l + \qquad (1)$$
$$+ x_{Ba}x_Y \sum_m (A_m^{BaY} + TB_m^{BaY} + TC_m^{BaY} \ln T)(x_Y - x_{Ba})^m +$$
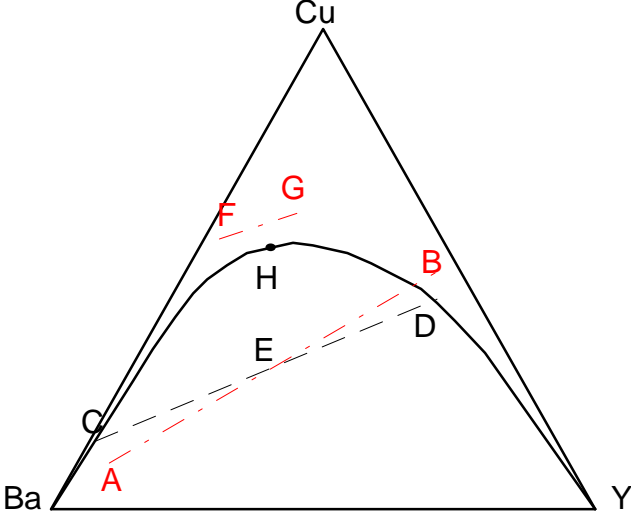$$+ x_{Ba}x_{Cu}x_Y (A^{BaCuY} + TB^{BaCuY} + TC^{BaCuY} \ln T)$$

Fig. 1. A miscibility gap in the ternary system. AB, FG are the experimental tie-lines, CD is the calculated tie-line, H is the critical point.

with the binary and ternary interaction parameters. Note that in Eq. (1) there are two independent variables only and the mole fractions of copper and yttrium, x_{Cu} and x_Y will be used as such below. The binary interaction parameters of the Ba-Cu and Cu-Y liquid alloys have been determined elsewhere [3, 4] (see Table 1). The Ba-Y binary interaction parameters and the Ba-Cu-Y ternary parameters are not known and the experimental tie-lines in the ternary miscibility gap at 1273 K [7] was utilized to determine them.

Each experimental tie-line connects two coexisting compositions of the liquid alloys (line AB in Fig. 1): $\{x'_{Cu,i}, x'_{Y,i}\} - \{x''_{Cu,i}, x''_{Y,i}\}$. It should be expected that because of measurement errors the calculated tie-lines (line CD in Fig. 1): $\{x'^{,calc}_{Cu,i}, x'^{,calc}_{Y,i}\} - \{x''^{,calc}_{Cu,i}, x''^{,calc}_{Y,i}\}$ will be different from the experimental ones to some extent.

To determine the unknowns interaction parameters (denoted as vector $\vec{\Theta}$ below) in the Gibbs energy of the melt (1), the sum of squared distances between the experimental and calculated tie-lines was minimized

$$\text{SS} = \sum_i [(x'_{Cu,i} - x'^{,calc}_{Cu,i})^2 + (x''_{Cu,i} - x''^{,calc}_{Cu,i})^2 + (x'_{Y,i} - x'^{,calc}_{Y,i})^2 + (x''_{Y,i} - x''^{,calc}_{Y,i})^2], \quad (2)$$

where the squared lengths of segments AC and BD for each tie-line are summed. The coordinates of the calculated tie-lines with the current set of the interaction parameters (vector $\vec{\Theta}$ is given) were found by solving the system of the non-linear equations

$$\mu_{Ba}(T, x'^{,calc}_{Cu,i}, x'^{,calc}_{Y,i}, \vec{\Theta}) = \mu_{Ba}(T, x''^{,calc}_{Cu,i}, x''^{,calc}_{Y,i}, \vec{\Theta}),$$
$$\mu_{Cu}(T, x'^{,calc}_{Cu,i}, x'^{,calc}_{Y,i}, \vec{\Theta}) = \mu_{Cu}(T, x''^{,calc}_{Cu,i}, x''^{,calc}_{Y,i}, \vec{\Theta}), \qquad (3a)$$
$$\mu_{Y}(T, x'^{,calc}_{Cu,i}, x'^{,calc}_{Y,i}, \vec{\Theta}) = \mu_{Y}(T, x''^{,calc}_{Cu,i}, x''^{,calc}_{Y,i}, \vec{\Theta}),$$

$$\frac{\frac{1}{2}\left(x''_{Cu,i} - x'_{Cu,i}\right) - x'^{,calc}_{Cu,i}}{x''^{,calc}_{Cu,i} - x'^{,calc}_{Cu,i}} = \frac{\frac{1}{2}\left(x''_{Y,i} - x'_{Y,i}\right) - x'^{,calc}_{Y,i}}{x''^{,calc}_{Y,i} - x'^{,calc}_{Y,i}}. \qquad (3b)$$

Determining four unknown coordinates of the tie-line to be calculated can not be done from the equilibrium criterion for two coexisting melts L_1 and L_2 (Eqs. 3a) only and in addition Eq. (3b) was employed. The latter sets a somewhat arbitrary condition that the calculated tie-line must pass the midpoint of the experimental tie-line (point E in Fig. 1).

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Table 1. Auxiliary binary interaction parameters

(the Gibbs energy in $J \cdot mol^{-1}$)

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	A_0	A_1	B_0	B_1	C_0	C_1
Ba-Cu [3]	−7191	0	3.363	0	0	0
Cu-Y [4]	−82460	38480	14.74	−6.607	0	0

During minimization of (2) under some set of values of the interaction parameters such a situation is possible when the calculated tie-line complying with condition (3d) can not be drawn (for instance, see the experimental tie-line FG in Fig. 1). It means that in this case the system of equations (3) is getting incompatible, and to cope with it, the critical point (point H in Fig. 1) was used instead of the both ends of the calculated tie-line (the squared distances FH and GH are to be substituted in Eq. 2 for the tie-line FG). The position of the critical point under the given vector $\vec{\Theta}$ was found by using the criterion for the critical point [8]

$$D = \begin{vmatrix} \dfrac{\partial^2 G}{\partial x_{Cu}^2} & \dfrac{\partial^2 G}{\partial x_{Cu}\partial x_Y} \\ \dfrac{\partial^2 G}{\partial x_{Cu}\partial x_Y} & \dfrac{\partial^2 G}{\partial x_Y^2} \end{vmatrix} = 0, \qquad D' = \begin{vmatrix} \dfrac{\partial D}{\partial x_{Cu}} & \dfrac{\partial D}{\partial x_Y} \\ \dfrac{\partial^2 G}{\partial x_{Cu}\partial x_Y} & \dfrac{\partial^2 G}{\partial x_Y^2} \end{vmatrix} = 0 \qquad (4)$$

The system of equations (3) was solved numerically by minimizing the sum of residual squares using the finite difference Levenberg-Marquardt algorithm. If the final sum of residual squares was not equal to zero, the incompatibility of equations (3) had been assumed and the position of the critical point was used as the coordinates of the calculated tie-line. The Levenberg-Marquardt method is designed for the unconstrained minimization but according to the definition of the mole fraction the values of x_{Cu} and x_Y must be inside of the open triangular simplex. To this end, the transformation of the open triangular simplex to the two-dimensional plane was applied as described below.

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Table 2. Recommended interaction parameters

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source	A_0^{BaY} $J \cdot mol^{-1}$	B_0^{BaY} $J \cdot K^{-1} \cdot mol^{-1}$	A^{BaCuY} $J \cdot mol^{-1}$
[6]	77000	0	0
[2]	200700	−22.3	0
present work	85960	0	0

The number of unknown interaction parameters in Eq. (1) was varied and with each given numbers of the unknowns the sum of squares (2) has been minimized. The solution with only one unknown interaction parameter, A_0^{BaY}, has been finally chosen as recommended. Adding of other Ba-Y binary and ternary parameters as unknowns did not lead to significant decrease in the minimal residual sum of squares (2).

The literature and recommended values for the interaction parameters are presented in Table 2 and Fig. 2 furnishes the final description of the miscibility gap.

3. Transforming the open triangular simplex to the two-dimensional plane

As was mentioned above, the mole fractions of two components of the ternary melt must be inside of the open triangular simplex

$$x_1 > 0, \; x_2 > 0, \; x_1 + x_2 < 1. \tag{5}$$

It is worth noting that in the general case the closed simplex has to be used, *i.e.* the signs $\geq$ and $\leq$ should stay instead of $>$ and $<$. This is necessary to guarantee the continuos transfer from a ternary system to the binaries and to pure substances. However in our case, the binaries were processed independently from the ternary system and for the sake of simplicity the condition (5) has been employed just as the open simplex.

The transformation based on the logistic function (the latter enjoys widespread use in the neural networks, see, for example Ref. [9]) has been developed by us as follows

$$\begin{cases} z_1 = \ln \dfrac{x_1(1 + a)}{1 + x_1(1 + a)} \\ z_2 = \ln \dfrac{x_2(1 + a)}{1 + x_2(1 + a)} \end{cases}, \qquad a = \begin{cases} x_1 / x_2, & x_1 \leq x_2 \\ x_2 / x_1, & x_1 > x_2 \end{cases} \tag{6}$$

It puts one-to-one any point from inside the triangular simplex (5) to the point on the two-dimensional plane ($-\infty < z < +\infty$) and thus allow us quite easily to convert the solution of the equations (3) to the task of the unconstrained minimization. The invert transformation can simply be written as follows

$$\begin{cases} x_1 = \left[(1 + a)\left(1 + e^{-z_1}\right) \right]^{-1} \\ x_2 = \left[(1 + a)\left(1 + e^{-z_2}\right) \right]^{-1} \end{cases}, \tag{7}$$

and moreover, both direct and invert transformation possess continuos derivatives.

The functions written on C++ and implementing the direct (6) and invert (7) transformation and also the first derivatives of the invert transformation are available on World-Wide-Web Service System [10].

4. Computing the equilibrium composition in the Ba-Cu-Y ternary system

After the Gibbs energies of all the phases in the Ba-Cu-Y system have been determined, the complete ternary phase diagram can be drawn. However in contrast to binaries, it is impossible to make a convenient graphical representation of the complete ternary phase diagram that can be utilized in all practically important cases. The only conceivable solution is employing a computer program which will compute the equilibrium composition in the ternary system at any given temperature and element composition "on the fly". In our case, the calculation of the equilibrium composition reduces to the constrained minimization of the total Gibbs energy as follows
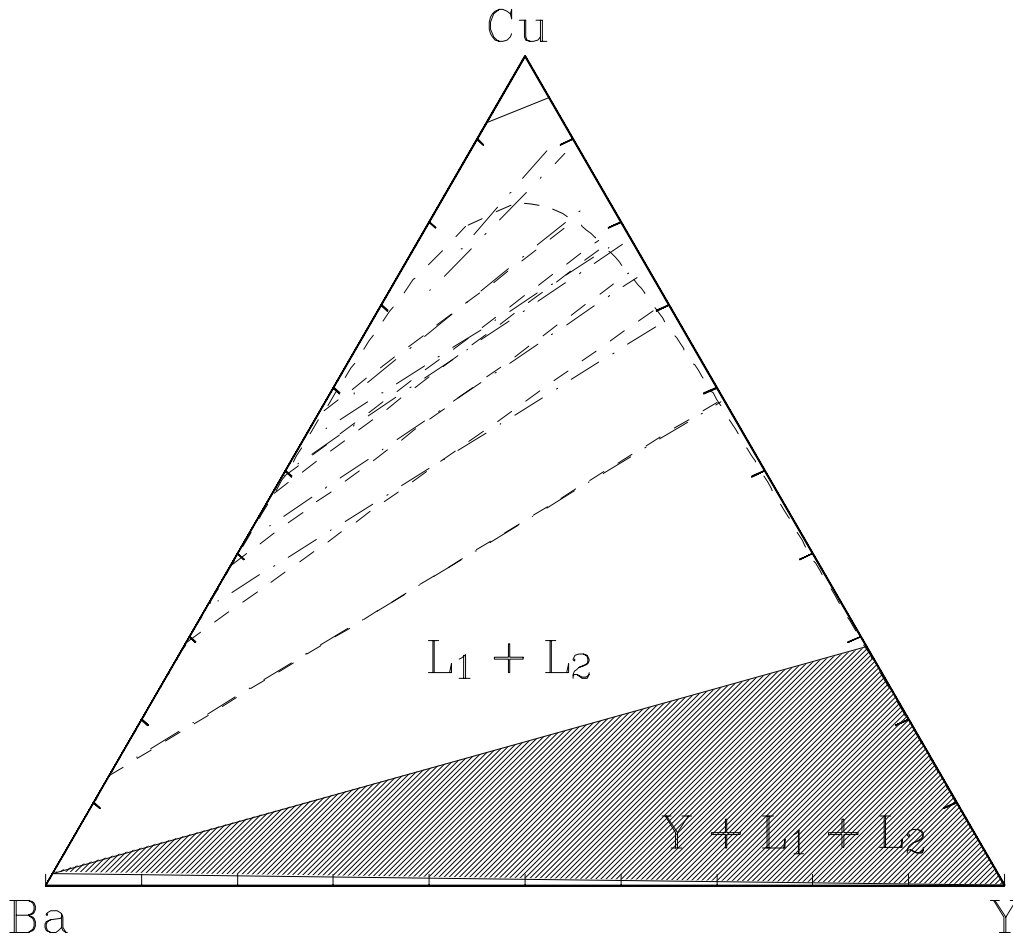
Fig. 2. The miscibility gap in the Ba-Cu-Y ternary system at 1273 K.
$-\cdot-\cdot-$ - the experimental tie-lines [7], $-----$ - the calculated tie-lines.

$$G = \Sigma_i n_i G_{m,i}(T) + n_{L1} G_{m,L1}(T, x'_{Cu}, x'_Y) + n_{L2} G_{m,L2}(T, x''_{Cu}, x''_Y) \qquad (8)$$

$$\Sigma_i a_{ki} n_i + n_{L1} x'_k + n_{L2} x''_k = b_k \qquad (9)$$

$$n_i \geq 0, \; n_{L1} \geq 0, \; n_{L1} \geq 0 \qquad (10)$$

where the sum over *i* includes the mole numbers and the molar Gibbs energies of ten solid stoichiometric phases (Ba, Cu, Y, BaCu, $BaCu_{13}$, Cu_6Y, Cu_4Y, Cu_7Y_2, Cu_2Y, CuY), and two terms for the melt reflect the possibility of the miscibility gap. The molar Gibbs energies of the melts, $G_{m,L1}$ and $G_{m,L2}$, are identical by themselves but it may happen that at some temperature and element composition both mole numbers n_{L1} and n_{L2} will be non-zero simultaneously and at the same time the compositions of the melts L_1 and L_2 will be different.

In all, the Gibbs energy of the Ba-Cu-Y system (8) depends on 16 unknowns (12 mole numbers for the phase amounts and 4 mole fractions to describe two compositions of the melt) subject to equality (9) and inequality (10) constraints. Three equations (9) express the mass conservation law - the total amounts of barium, copper and yttrium must be constant (*k* enumerates elements and a_{ki} is equal to the index of the *k*-th element in the *i*-th compound). Equation (10) asserts that amounts of phases must be non-negative. Besides constraints (9) and (10) there is the condition on the range of mole fraction values - the open triangular simplex (5). However, the latter can be taken out by the transformations (6) and (7) that simplifies in some extent the minimization of (8).

The Gibbs energies of the pure elements [11] and the thermodynamic properties of the stoichiometric compounds [3, 4] used for computing the Ba-Cu-Y phase diagram in the present work are given in Tables 3 and 4.

Table 3. Gibbs energies of the pure elements [11]

$$G/J \cdot mol^{-1} = a + bT + cT\ln T + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9}$$

	T/K	a	b	c	d	e	f
Ba, bcc	298.15 – 1000	−17685.226	233.78606	−42.889	−1.8314e-3	−0.000095e-6	705880
Ba, bcc	1000 – 2995	−64873.614	608.188389	−94.2824199	19.504772e-3	−1.051353e-6	8220192
Ba, l	298.15 – 1000	−9738.988	229.540143	−43.4961089	−2.346416e-3	0.991223e-6	723016
Ba, l	1000 – 2995	−7381.093	235.49642	−45.103	2.154e-3	0.000027e-6	−365
Cu, fcc	298.15 – 1357.77	−7770.458	130.485235	−24.112392	−2.65684e-3	0.129223e-6	52478
Cu, fcc[a]	1357.77 – 3200	−13542.026	183.803828	−31.38	0	0	0
Cu, l[b]	298.15 – 1357.77	5194.277	120.973331	−24.112392	−2.65684e-3	0.129223e-6	52478
Cu, l	1357.77 – 3200	−46.545	173.881484	−31.38	0	0	0
Y, hcp	298.15 – 1500	−7347.055	117.532124	−23.8685	−3.845475	0.011125e-6	−16486
Y, hcp	1500 – 1752	−15802.62	229.831717	−40.2851	6.8095e-3	−1.14182e-6	0
Y, bcc	1752 – 1799	−10207.724	195.741984	−35.0201	0	0	0
Y, bcc	1799 – 3700	104813.954	−386.167564	39.8075986	−19.918739e-3	0.841308e-6	−31549963
Y, l	298.15 – 1799	3934.121	59.921688	−14.8146562	−15.623487e-3	1.442946e-6	−140695
Y, l	1799 – 3700	−13337.609	258.004539	−43.0952	0	0	0

[a] $h = 3.642e29$, [b] $g = -5.849e-21$

The minimization of (8) with equality and inequality constraints is a task of non-linear program-ming, and to this end, the subroutine DONLP (DO Non-Linear Programming) [12-13] has been utilized. Our experience has showed that the DONLP is working fairly well with the tasks like the minimization of (8). A good starting point, that is typical for all optimization routines, is essential for the DONLP to be successful. For that purpose, the linear programming estimates have been applied in the present work when the function (8) approximated by the equation

$$G \approx \Sigma_i n_i G_{m,i}(T) + \Sigma_j n_j G_L(T; x_{Cu,j}, x_{Y,j}) \qquad (11)$$

In Equation (11), the melt is considered as a set of the "point" phases chosen on the Gibbs triangle according to the grid. It has been found that the good starting point to make DONLP work is achieved by the grid with the composition changed by 2 mole per cent (approximating the melt by 1326 "point" phases). The minimization of (11) is a typical linear programming problem and it can be easily solved by the standard subroutines.

The program BACUY_EQ.EXE for MS-DOS to compute the equilibrium composition for the Ba-Cu-Y system is available on World-Wide-Web Service System [10]. The program is kind of shell to our Gibbs energies and the subroutine DONLP.

5. Discussion

The thermodynamic assessment of the Ba-Cu-Y ternary system has been done previously in Refs. [2, 6]. The layout of the investigations was the same. First, the Ba-Cu and Cu-Y binaries were optimized. Then after using the experimental values from the ternary system, the Gibbs energies of the ternary liquid alloys and of the Ba-Y binary melt were determined. In Ref. [2, 6], as in the present work, the zero values for the ternary interaction parameters have been recommended (see Table 4).

The first assessment of the Ba-Cu-Y system has been performed in Ref. [6]. However, the authors of [6] have obtained non-optimum description of the Ba-Cu and Cu-Y binary phase diagrams (see discussion and figures in Ref. [3, 4]) and hence their Gibbs energies of the phases in the binaries are not reliable. As a result, the prediction of Ref. [6] on triangulation of the subsolidus part of the ternary phase diagram happened to be incorrect (see discussion in Ref. [2]). Also, the authors of [6] could not have obtained the satisfactory description for the experimental tie-lines in the miscibility gap of the isothermal cross section of the ternary system at 1273 K (see Fig. 8 in Ref. [6]). It should be specially stressed that in spite of the proximity between the Ba-Y binary interaction parameters, A_0^{BaY} in Ref. [6] and in the present work (see Table 4) the recommended Ba-Cu-Y ternary phase diagrams are quite different because of the big differences in the Gibbs energies in the Ba-Cu and Cu-Y binaries.

The description of the Ba-Cu and Cu-Y phase diagrams in Ref. [2] and in our works [3, 4] is pretty close and the same can be said about the corresponded Gibbs energies. The main difference in the present work as compared with Ref. [2] is the huge difference in the Ba-Y binary interaction parameters (see Table 2).

Table 4. Thermodynamic properties of reactions

$$\frac{m}{m+n} A(s) + \frac{n}{m+n} B(s) = \frac{1}{m+n} A_m B_n(s)$$

	ΔH $J \cdot mol^{-1}$	ΔS $J \cdot K^{-1} \cdot mol^{-1}$
BaCu	–2594.	0
$BaCu_{13}$	–924.6	0
Cu_6Y	–12610	0
Cu_4Y	–16560	0
Cu_7Y_2	–17280	0
Cu_2Y	–20100	0
CuY	–20180	0

Fig. 3 displays the Ba-Y miscibility gap as predicted by the values of the Ba-Y interaction parameters in Refs. [2, 6] and in the present work. The results of Ref. [2] lead to the critical temperature of about 12000 K and predict that the mutual solubility of liquid barium and yttrium at 2000 K is less than 10^{-3} mole per cent. In our opinion, such predictions are physically unreasonable. The interaction parameter, A_0^{BaY} determined in the present work gives the critical temperature of about 5000 K and the mutual solubility about 1 mole per cent at 2000 K. The latter values are still a bit extreme if compared with miscibility gaps in other binaries but are much reasonable than according to Ref. [2].

In Ref. [2], the experimental values from the Ba-Cu-Y ternary system was employed to determine the unknown Ba-Y interaction parameters. but in contrast with the present work, this was done by "error and trial" method without setting up a formal optimization task. The main reason for such a high value of the parameter A_0^{BaY} in Ref. [2] has been the assignment of the peak on the DTA curve at 1136 K for the compositions of the ternary
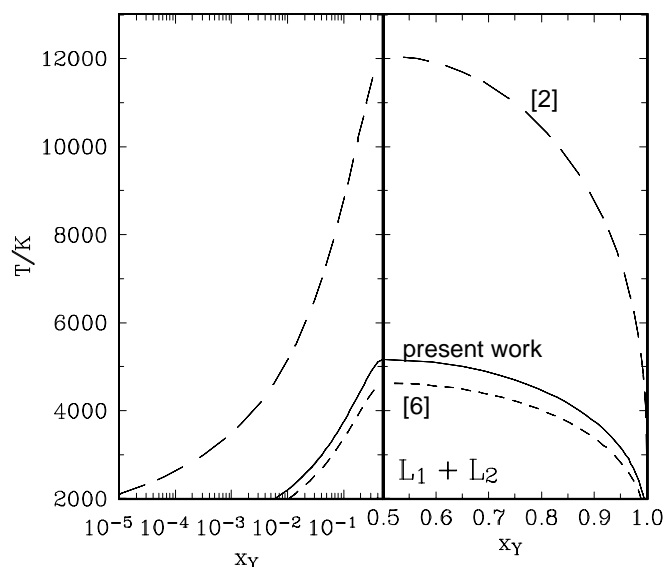
Fig. 3. The miscibility gap in the Ba-Y binary as predicted after the assessment of the ternary system (the gas phase is excluded).

system closed to copper to the reaction

$$L'' = L' + Cu + Cu_6Y \qquad (12)$$

However, the peak of 1136 K on the DTA curve [2] can be interpreted differently and in accordance to the Gibbs energies determined in the present work. To demonstrate it, the equilibrium heating-cooling curves according to the models of Ref. [2] and the present work have been computed (see Fig. 4 and 5).

On the whole, the difference between the present work and Ref. [2] is that the miscibility gap in the isothermal cross section of the ternary phase diagram according to Ref. [2] is more extended toward copper. For instance, according to Ref. [2] the miscibility gap is still exist in the melts containing 84.5 mole per cent of copper but according to the present model it is already completed (see Fig. 4). For the compositions with lower copper content there is no qualitative difference between these two models (see Fig. 5).

Fig. 4 and 5 show that the experimental DTA peaks are reproduced by both models with the same accuracy (±25 K) and the difference lays in the interpretation of the peak at 1136 K. If in Ref. [2] the peak is ascribed to Reaction (12), in out model it can be interpreted as the beginning of the crystallization of the solid phase Cu_6Y.

In conclusion it must be mentioned that the biggest uncertainty in the assessment of the Ba-Cu-Y phase diagram now is the lack of experimental values for the Ba-Y binary.
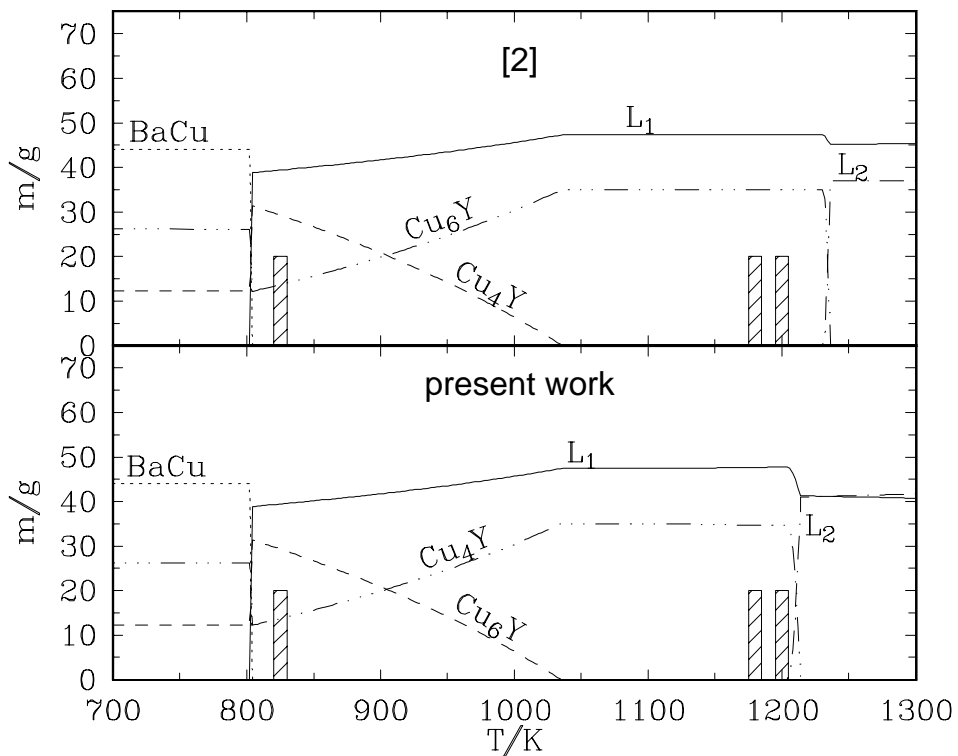
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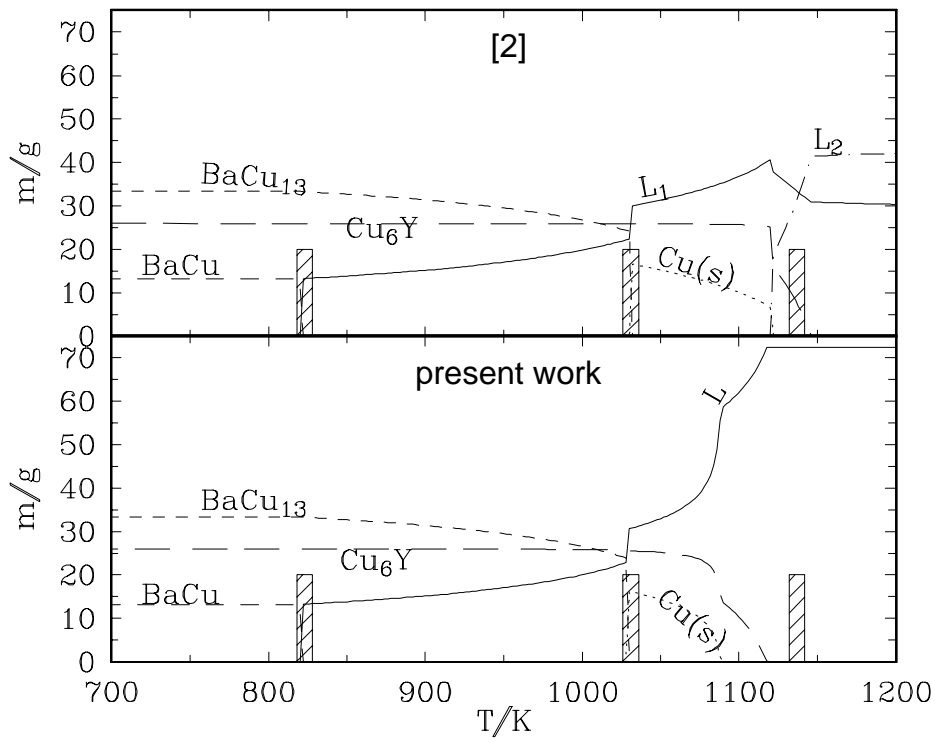
Fig. 4. **The mass of phases in equilibrium as a function of temperature for the composition** 0.1 Ba + 0.845 Cu + 0.055 Y. **The hatched bars shows the experimental peaks on the DTA curves.**

Fig. 5. **The mass of phases in equilibrium as a function of temperature for the composition** 0.219 Ba + 0.679 Cu + 0.102 Y. **The hatched bars shows the experimental peaks on the DTA curves.**

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