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 optimization and calculation of the ternary phase diagrams significantly is suggested. The literature and present results are discussed.

1. Introduction

The present work is a part of the project 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 in order to find a metallic precursor for producing the superconductors (see Ref. [1] for discussion).

The optimization of the Ba-Cu and Cu-Y binary phase diagrams was made by us earlier [2, 3]. There are no any experimental values for the Ba-Y phase diagram. According to Refs. [4, 5] 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 [6] 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 [6] and thermodynamic properties of the phases in the Ba-Cu and Cu-Y binaries [2, 3] 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

$$\Delta_{mix}G(T, x_{Cu}, x_Y) = x_{Ba} RT \ln x_{Ba} + x_{Cu} RT \ln x_{Cu} + x_Y RT \ln x_Y +$$

$$+ x_{Ba} x_{Cu} \sum_k (A_k^{BaCu} + T B_k^{BaCu} + T C_k^{BaCu} \ln T)(x_{Cu} - x_{Ba})^k +$$

$$+ x_{Cu} x_Y \sum_l (A_l^{CuY} + T B_l^{CuY} + T C_l^{CuY} \ln T)(x_Y - x_{Cu})^l + \qquad (1)$$

$$+ x_{Ba} x_Y \sum_m (A_m^{BaY} + T B_m^{BaY} + T C_m^{BaY} \ln T)(x_Y - x_{Ba})^m +$$

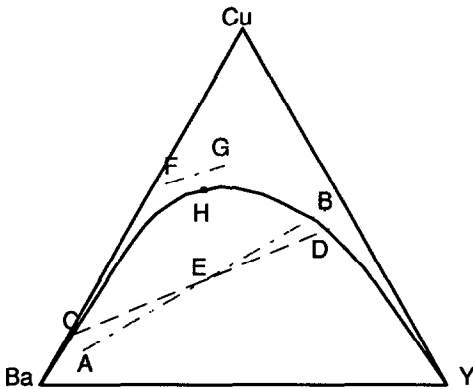$$+ x_{Ba} x_{Cu} x_Y (A^{BaCuY} + T B^{BaCuY} + T C^{BaCuY} \ln T)$$

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 [2, 3] (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 [6] 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 $\bar\Theta$ below) in the Gibbs energy of the melt (1), the sum of squared distances between the experimental and calculated tie-lines was minimized

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

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 $\bar\Theta$ is given) were found by solving the system of the non-linear equations

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

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

$$\mu_Y(T, x'^{,calc}_{Cu,i}, x'^{,calc}_{Y,i}, \bar\Theta) = \mu_Y(T, x''^{,calc}_{Cu,i}, x''^{,calc}_{Y,i}, \bar\Theta),$$

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

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

Table 1. Auxiliary binary interaction parameters

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

	A_0	A_1	B_0	B_1	C_0	C_1
Ba-Cu [2]	−7191	0	3.363	0	0	0
Cu-Y [3]	−82460	38480	14.74	−6.607	0	0

a somewhat arbitrary condition that the calculated tie-line must pass the midpoint of the experimental tie-line (point E in Fig. 1).

During minimization of (2) under some set of values of the interaction parameters a situation may occur 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 $\bar{\Theta}$ was found by using the criterion for the critical point [7]

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

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.

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 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.

Table 2. Recommended interaction parameters

source	A_0^{BaY} $J \cdot mol^{-1}$	B_0^{BaY} $J \cdot K^{-1} \cdot mol^{-1}$	A^{BaCuY} $J \cdot mol^{-1}$
[5]	77000	0	0
[1]	200700	−22.3	0
present work	85960	0	0

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 continuous transfer from a ternary system to the binaries and to pure components. 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. [8]) 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 transformations possess continuous derivatives.

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

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

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

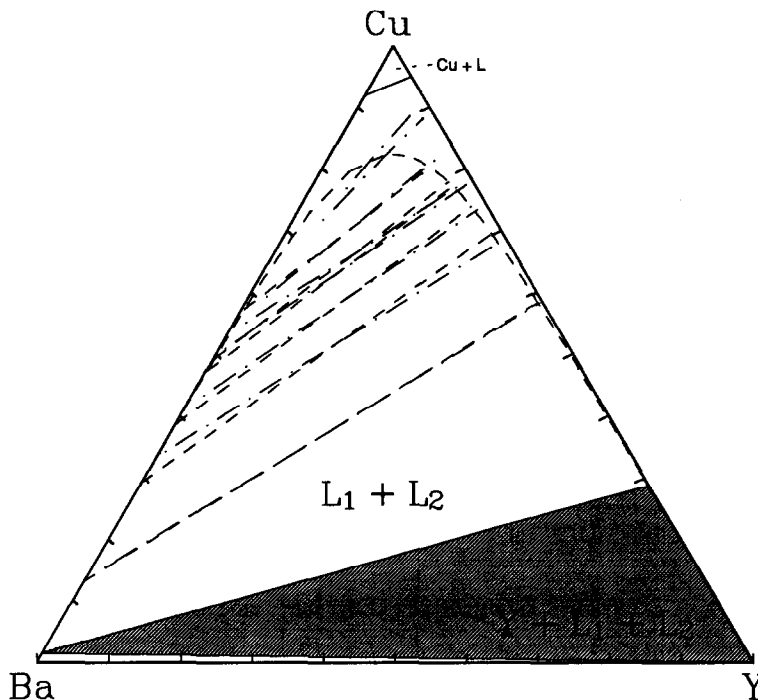$$n_i \geq 0, n_{L1} \geq 0, n_{L2} \geq 0 \tag{10}$$

Fig. 2. The miscibility gap in the Ba-Cu-Y ternary system at 1273 K. — · — · — - the experimental tie-lines [6], — — — — - the calculated tie-lines, ——— extent of the calculated miscibility gap.

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 [9] and the thermodynamic properties of the stoichiometric compounds [2, 3] used for computing the Ba-Cu-Y phase diagram in the present work are given in Tables 3 and 4.

The minimization of (8) with equality and inequality constraints is a task of non-linear programming, and to this end, the subroutine DONLP (DO Non-Linear Programming) [10-11] 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

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

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 (http://www.chem.msu.su/people/rudnyi/bacuy/welcome.html). 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. [1, 5]. 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. [1, 5], as in the present work, the zero values for the ternary interaction parameters have been recommended (see Table 4).

Table 3. Gibbs energies of the pure elements [9]

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

|	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

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$_6$Y	−12610	0
Cu$_4$Y	−16560	0
Cu$_7$Y$_2$	−17280	0
Cu$_2$Y	−20100	0
CuY	−20180	0

The first assessment of the Ba-Cu-Y system has been performed in Ref. [5]. However, the authors of [5] have obtained non-optimum description of the Ba-Cu and Cu-Y binary phase diagrams (see discussion and figures in Ref. [2, 3]) and hence their Gibbs energies of the phases in the binaries are not reliable. As a result, the prediction of Ref. [5] on triangulation of the subsolidus part of the ternary phase diagram happened to be incorrect (see discussion in Ref. [1]). Also, the authors of [5] 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. [5]). It should be specially stressed that in spite of the proximity between the Ba-Y binary interaction parameters, A_0^{BaY} in Ref. [5] 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 second assessment has been made in Ref. [1] where new DTA experiments have been carried out for the eleven samples of the Ba-Cu-Y ternary system. The authors of Ref. [1] have suggested a set of reactions in order to explain the experimental peaks on the DTA heating and cooling curves. Then they assessed the Ba-Cu-Y ternary melt by "trial and error" based on the assignment of the T_2 peak on the DTA curves at 1136 K for the compositions of the ternary system close to copper to the reaction

$$L'' = L' + Cu + Cu_6Y \qquad (12)$$
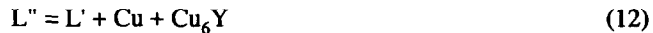
(the results of Ref. [6] have been discarded). The overall description of the DTA peaks by the thermodynamic model obtained was fairly good, however this has exacted the huge Ba-Y binary interaction parameter (see Table 2).

Fig. 3 displays the Ba-Y miscibility gap as predicted by the values of the Ba-Y interaction parameters in Refs. [1, 5] and in the present work. The results of Ref. [1] lead to the critical temperature of about 12000 K, predict that the mutual solubility of liquid barium and yttrium at 2000 K is less than 10^{-3} mole per cent and the solubility of yttrium in liquid barium at 1500 K is less than 10^{-5} 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, the mutual solubility about 1 mole per cent at 2000 K and the solubility of yttrium in liquid barium at 1500 K about 0.1 mole per cent. The latter values are still a bit extreme if compared with miscibility gaps in other binaries but are much more reasonable than according to the thermodynamic model recommended in Ref. [1].

The latter was the main reason why the experimental results obtained in Ref. [1] have not been used in our assessment directly. Yet, after the new model of the Ba-Cu-Y melt has been assessed in the present work, the equilibrium heating-cooling curves for all the samples measured in Ref. [1] have been computed according to our model (two typical curves are shown on Fig. 4 and 5). The quantitative description of the DTA peaks by our model is worse than by the model derived in Ref. [1] but the overall agreement can be perceived as satisfactory (note that the experimental peaks have not been used in the assessment). According to the model suggested in the present work the reaction (12) does not exist at all, and the T_2 peak on the DTA curves at 1136 K can be explained for different compositions differently, either as liquidus or as the beginning of the ternary monovariant reaction
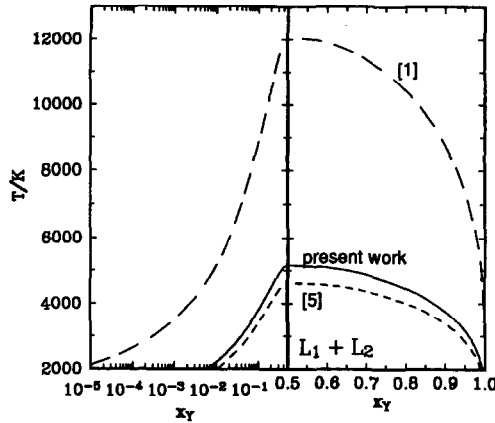
$$L \rightarrow Cu + Cu_6Y$$
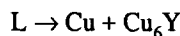
Fig. 3. The miscibility gap in the Ba-Y binary as predicted
after the assessment of the ternary system (the gas phase is
excluded).

On the whole, the difference between the present work and Ref. [1] is that the miscibility gap in the isothermal cross section of the ternary phase diagram according to Ref. [1] is more extended toward copper. For instance, according to Ref. [1] the miscibility gap still exists in the melts containing 84.5 mole per cent of copper but according to the present model it is already closed (see Fig. 4). For the compositions with lower copper content there is no qualitative difference between these two models (quantitative difference is within 20 K). It should be especially mentioned that the difference between our models does not affect the conclusion made in Ref. [1] about fundamental problems for various liquid phase processes in order to obtain a metallic "YBa2Cu3" precursor (see Section 7 in Ref. [1]).

Finally, 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. The most valuable information in order to discriminate the two thermodynamic models would be the experimental solubility of yttrium in liquid barium at any temperature.
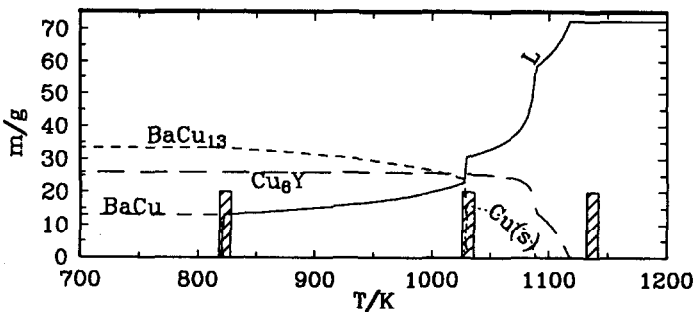

Fig. 4. The mass of phases in equilibrium as a function of temperature for the composition 0.1 Ba + 0.845 Cu + 0.055 Y as predicted by the thermodynamic model obtained in the present work. The hatched bars shows the experimental peaks on the DTA curves [1].
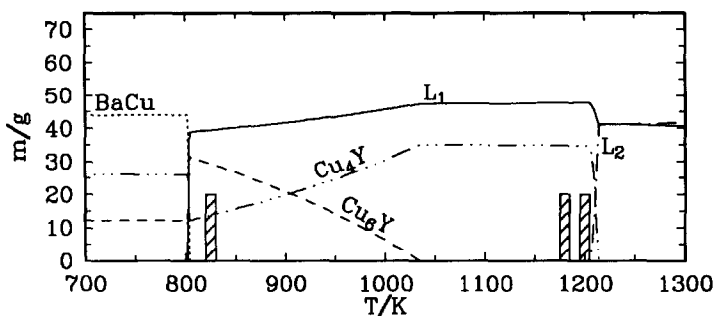
Fig. 5. The mass of phases in equilibrium as a function of temperature for the composition 0.219 Ba + 0.679 Cu + 0.102 Y as predicted by the thermodynamic model obtained in the present work. The hatched bars shows the experimental peaks on the DTA curves [1].

Acknowledgments

References

1. R. Konetzki, R. Schmid-Fetzer, S. Fries, H.L. Lukas. Z. Metallkd., 85, 748 (1994).

2. E.B. Rudnyi. Zh. Fiz. Khim., 70, 986 (1996), English translation in Rus. J. Phys. Chem.

3. E.B. Rudnyi. Zh. Fiz. Khim., 70, 1007 (1996), English translation in Rus. J. Phys. Chem.

4. T.D. Dzhuraev, R.T. Altynov. Dokl. Akad. Nauk Tadzhikskoi SSR, 29, 472 (1986).

5. S. an Mey, K. Hack, K. Itagaki, P.J. Spencer, D. Neuschutz. CALPHAD, 14, 175 (1990).

6. K. Itagaki. Unpublished work, cited according to [5].

7. J.W. Gibbs. Trans. Connect. Acad. 3, 108 (1876), 3, 343 (1878).

8. P.A. Jansson. Anal. Chem. 63, 357A (1991).

9. Dinsdale A.T. CALPHAD. 15, 317 (1991).

10. P. Spellucci. Lect. Notes. Control and Inf. Sci. 30, 123 (1980).

11. P. Spellucci. Subroutine DONLP, available at NETLIB in the directory OPT. e.g. ftp://netlib2.cs.utk.edu/opt or http://www.netlib.org/opt/