CALCULATION OF SUBSOLIDUS PHASE RELATION DIAGRAMS OF Y–Ba–Cu–O SYSTEM①

Zhang Hengzhong②, Zhang Pingmin③, Chen Xinmin④

Central South University of Technology, Changsha 410083, China

ABSTRACT

Mathematical principle and method for the calculation of subsolidus phase relation diagrams of the quasi–ternary system $YO_{1.5}$–BaO–CuO were developed, and the corresponding mathematical model was established. Subsolidus phase relation diagrams of this system at different temperatures were calculated from thermodynamic data. The calculated results showed that in Y–Ba–Cu–O system $BaCuO_2$ and Y_2BaCuO_5 are thermodynamically stable at room–temperature, and $Y_2Cu_2O_5$ and $YBa_2Cu_3O_{6.5}$ also become stable at temperatures higher than 300℃ and 750℃ respectively. The calculated results are in good agreement with those from experiments.

Key words: superconductor, yttrium-barium-copper-oxygen system, phase diagrams

1 INTRODUCTION

Y–Ba–Cu–O system is of major importance among the high T_c superconductor oxide systems. A number of complicated phase transformations occur in the synthesis of so-called 123 superconductor phase ($YBa_2Cu_3O_{7-y}$). A lot of binary and ternary complex oxides exist in the system. Mathematical principle and method for the calculation of subsolidus phase relation diagrams of Y–Ba–Cu–O system were developed in present work, and the subsolidus phase relation diagrams of the quasi-ternary system $YO_{1.5}$–BaO–CuO at different temperatures were calculated with the thermodynamic data of the compounds $Y_2Cu_2O_5$, $BaCuO_2$, $YBa_2Cu_3O_{6.5}$, and Y_2BaCuO_5(i.e. the so-called 211 phase) evaluated from calorimetric determinations and entropy estimations by the authors. The work is helpful to people not only in understanding the formation and the structural chemistry of the YBCO single phase (123 phase) but also in introducing an auxiliary phase such as the 211 one into YBCO in order to increase its current capacity.

2 PRINCIPLE AND METHOD FOR CALCULATION

According to thermodynamic principle the general condition for thermodynamic equilibrium at constant temperature and pressure is that total free energy G of the system should be at a minimum[1], namely:

$$G_{\min} = minimized\ (G) \quad (1)$$

Let n_{10}, n_{20} and n_{30} represent respectively

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②Dr; ③Professor; ④Professor, Academician

the initial molar numbers of $YO_{1.5}$, BaO and CuO in the quasi-ternary system $YO_{1.5}$–BaO –CuO; n_i and G_i (where i = 1, ···, 7) represent respectively the molar number and Gibbs free energy of $YO_{1.5}$, BaO, CuO, $Y_2Cu_2O_5$, $BaCuO_2$, $YBa_2Cu_3O_{6.5}$ and Y_2BaCuO_5.

Considering that Gibbs free energy G_i of the solid compound i at a certain temperature and normal pressure is approximately equals to its standard Gibbs free energy G_i^o at the same temperature, and the change of pressure produces no significant effects on Gibbs free energies of condensed phases, and assuming that there is no solid solution formed in the system, the total Gibbs free energy of the system is:

$$G = \sum_{i=1}^{7} n_i G_i = \sum_{i=1}^{7} n_i G_i^o \tag{2}$$

Based on the principle of minimizing Gibbs free energy and on the materials equilibria we obtain the mathematical model for the calculation of subsolidus phase relation diagrams of the quasi-ternary system $YO_{1.5}$– BaO –CuO:

$$\text{minimize } (n_1 G_1^\circ + n_2 G_2^\circ + \cdots + n_7 G_7^\circ) \tag{3}$$

subjecct to the constrains

$$n_1 + 2n_4 + n_6 + 2n_7 = n_{10} \tag{4}$$

$$n_2 + n_5 + 2n_6 + n_7 = n_{20} \tag{5}$$

$$n_3 + 2n_4 + n_5 + 3n_6 + n_7 = n_{30} \tag{6}$$

$$n_1, \cdots, n_7 \geqslant 0 \tag{7}$$

$$(n_{10}, \cdots, n_{30} \geqslant 0$$

Where formula (3) is the equation of minimal Gibbs free energy, formulas (4), (5) and (6) are respectively the material equilibrium equations of $YO_{1.5}$, BaO and CuO. Replacing n_1, n_2 and n_3 in (2) with those solved from equations (4) to (6), formula (2) can be simplified and rearranged as follows:

$$G = G_m^\circ + n_4 \Delta G_1^\circ + n_5 \Delta G_2^\circ + n_6 \Delta G_3^\circ + n_7 \Delta G_4^\circ \tag{8}$$

where G_m° is the standard Gibbs free energy of the initial mixture of $YO_{1.5}$, BaO and CuO:

$$G_m = n_{10} G_1^\circ + n_{20} G_2^\circ + n_{30} G_3^\circ$$

ΔG_1°, ΔG_2°, ΔG_3° and ΔG_4° are respectively the changes of standard Gibbs free energy of the following four reactions:

1 $$2YO_{1.5} + 2CuO = Y_2Cu_2O_5 \tag{9}$$

$$\Delta G_1^o = G_4^o - 2G_1^o - 2G_3^o$$

2 $$BaO + CuO = BaCuO_2 \tag{10}$$

$$\Delta G_2^o = G_5^o - G_2^o - G_3^o$$

3 $$YO_{1.5} + 2BaO + 3CuO = YBa_2Cu_3O_{6.5} \tag{11}$$

$$\Delta G_3^o = G_6^o - G_1^o - 2G_2^o - 3G_3^o$$

4 $$2YO_{1.5} + BaO + CuO = Y_2BaCuO_5 \tag{12}$$

$$\Delta G_4^o = G_7^o - 2G_1^o - G_2^o - G_3^o$$

Minimizing the value of formula (8) and considering the G_m° being a constant, the mathematical models (3)—(7) can be written as a typical form of linear programming[2] (see equations (13) to (15)).

$$\text{minimize } (n_4 \Delta G_1^o + n_5 \Delta G_2^o + n_6 \Delta G_3^o + n_7 \Delta G_4^o) \tag{13}$$

subject to the constrains

$$\begin{bmatrix} n_1 \\ n_2 \\ n_3 \end{bmatrix} + A \begin{bmatrix} n_4 \\ n_5 \\ n_6 \\ n_7 \end{bmatrix} = \begin{bmatrix} n_{10} \\ n_{20} \\ n_{30} \end{bmatrix} \tag{14}$$

$$n_1, \cdots, n_7 \geqslant 0 \tag{15}$$

with matrix A being

$$A=\begin{bmatrix}2&0&1&2\\0&1&2&1\\2&1&3&1\end{bmatrix}$$

The elements of matrix A in the first row represent respectively the numbers of the formula $YO_{1.5}$ contained in $Y_2Cu_2O_5$, $BaCuO_2$, $YBa_2Cu_3O_{6.5}$ and Y_2BaCuO_5, and the elements in the second and the third row represent the contained BaO and CuO respectively. Equations (13) to (15) can be solved with simplex algorithm for linear programming[2].

3 SELECTIONS OF THERMODYNAMIC DATA

Expressions of $\Delta G_1^\circ - \Delta G_4^\circ$ in (9)—(12) as the functions of temperature should be obtained prior to the calculation of subsolidus phase relation diagrams of the quasi-ternary system $YO_{1.5}$–BaO–CuO.

The standard enthalpies of formation for the compounds $Y_2Cu_2O_5$, $BaCuO_{2+x}$, $YBa_2Cu_3O_{7-y}$ and Y_2BaCuO_5 were determined calorimetrically by the authors through designing proper thermochemical circles, and their heat capacities were determined both with the dropping method of calorimetry and the DSC scanning method. Also the standard entropies of these compounds were estimated with the entropy estimation method for complex oxides developed by the authors in reference to the literature. The results are listed in Table 1[3,4]. Polynomials of $\Delta G_1^\circ - \Delta G_4^\circ$ as functions of temperature were derived according to the thermodynamic principle based on the data in Table 1, and were further changed by regression into their more commonly used forms (Table 2):

$$\Delta G^\circ = a + bT\ln T + cT$$

Such an equation can be used for calculation at temperatures properly extrapolated such as at 950℃. For comparison, equations of ΔG_i° from different authors are listed in Table 2 and shown in Fig.1.

Lee et al. obtained their results by optimazation calculation from some known phase relations in Y–Ba–Cu–O system based on the

Table 1 Thermodynamic data of related compounds in Y–Ba–Cu–O system

Substances	$\Delta_f H^\circ_{298}$ kJ · mol^{-1}	S°_{298} J · mol^{-1} · K^{-1}	A	B	C	D	Temp. Range	References
$YBa_2Cu_3O_{6.99}$	−2 659.31							[4]
$YBa_2Cu_3O_{6.90}$	−2 652.04	321.16*	333.97	−454.43	41.836	794.18	298–973	[4,*5]
$YBa_2Cu_3O_{6.77}$	−2 641.78							[4]
$YBa_2Cu_2O_{6.60}$	−2 627.90							[4]
$YBa_2Cu_3O_{6.50}$	−2 619.93	316.78	327.98	−455.27	42.171	794.18	298–973	[4]
$Y_2Cu_2O_5$	−2 198.64	219.19	149.82	113.02	0	0	298–973	[3,4]
Y_2BaCuO_5	−2 656.44	239.58	329.09	−361.56	−42.75	341.43	298–973	[4]
$BaCuO_{2.33}$	−788.59							[4]
$BaCuO_{2.42}$	−796.19		77.628	−14.018	18.141	130.85	289–973	[4]
$BaCuO_2$	−760.72	103.59	71.337	−14.897	18.493	130.85	289–973	[4]
O_2(g)	0	205.04	29.957	4.184	−1.674	0	298–3,000	[6]
Y_2O_3	−1,905.39	99.16	123.85	5.021	−20.00	0	298–1,330	[6]
BaO	−553.54	70.29	53.304	4.351	−8.301	0	298–1,270	[6]
CuO	−155.85	42.59	43.832	16.765	−5.883	0	298–1,359	[6]

Temp. Range in K is the temperature range within which the *Cp* formula can be applied,
$C_p = A + B \times 10^{-3}T + C \times 10^5 T^{-2} + D \times 10^{-6}T^2$ J · mol^{-1} · K^{-1}

Table 2 Standard Gibbs free energy changes of reactions 1 to 4 (J.mol^{-1})

Reaction	$\Delta G^o = f(T)$	Temp.range,K	Authors
1	$2YO_{1.5}+2CuO = Y_2Cu_2O_5$		
	$\Delta G_1^o = 19{,}805+6.695\ TInT-77.996\ T$	298–1,223	present work
	$\Delta G_1 = 14{,}092-20.942T$		Lee et al.*
	$\Delta G_1^o = -7{,}509-5.29T$	973–1173	Fan[7]
	$\Delta G_1^o = 10{,}910-13.41\ T$	1,097–1,292	Pankajavalli et al.[8]
	$\Delta G_1^o = -19{,}450+3.56\ T$	973–1,223	Wiesner et al.[9]
2	$BaO+CuO = BaCuO_2$		
	$\Delta G_2^o = -56{,}644-12.616\ TInT+98.15T$	298–1,223	present work
	$\Delta G_2^o = -17{,}620-10.472\ T$		Lee et al.*
	$\Delta G_2^o = -43{,}900+7.3\ T$	973–1,173	Fan[7]
3	$YO_{1.5}+2BaO+3CuO = YBa_2Cu_3O_{6.5}$		
	$\Delta G_3^o = -112{,}380-45.852\ TInT+325.30T$	298–1,223	present work
	$\Delta G_3^o = -143{,}640+48.5721\ T$		Lee et al.*
	$\Delta G_3^o = -94{,}571-18.8T$	973–1,173	Fan[7]
4	$2YO_{1.5}+BaO+CuO = Y_2BaCuO_5$		
	$\Delta G_4^o = -41{,}966-1.635\ TInT-17.316\ T$	298–1,223	present work
	$\Delta G_4^o = -76{,}023+11.3391\ T$		Lee et al.*
	$\Delta G_4^o = -44{,}892-28.50\ T$	973–1173	Fan[7]

* Lee B J, Lee D N. Thermodynamic Evaluation for Y–Ba –Cu –O System, private communication, (1989).

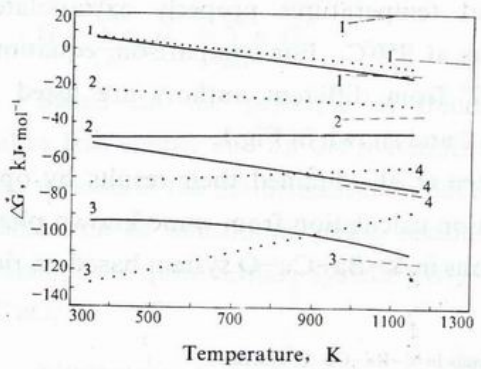

Fig. 1 Comparisons of ΔG_i^o by different authors

1—ΔG_1^o, 2—ΔG_2^o, 3—ΔG_3^o, 4—ΔG_4^o

——present work; · · · Lee et al.*; – – –Fan[7];

· — · — · Pankajavalli et al.[8]; — · · —Wiesner et al.[9]

sub-lattice model of ionic solutions, and both Fan[7] and Pankajavalli et al[8]. obtained their results through solid electrolyte method. It is demonstrated in Fig.1 that the results of ΔG^o for reaction 1 from different authors except Wiesner et al. are close, and for reactions 2 to 4 the results of Fan and the present work are very close too. Yet there exist great differences between the results of Lee et al. and those of both Fan and the present work. The largest deviations between Fan's results and those of the present work do not exceed 10 kJ · mol^{-1} within the temperature ranges of Fan's experiments. This proved the coincidences and the reliabilities of the results obtained by the two authors. Consequently the equations of ΔG^o in the present work will be used for the calculation of the subsolidus phase relation diagrams of the Y–Ba–Cu–O sysytem.

4 RESULTS AND DISCUSSION

A computer program for the calculation of subsolidus phase relation diagrams of the quasi–ternary system $YO_{1.5}$–BaO–CuO was coded with simplex algorithm for linear programming. One can consult the program flow chart and its list for reference[4].

Figs. 2–4 show the calculated subsolidus phase relation diagrams of the quasi-ternary system $YO_{1.5}$–BaO–CuO at different temperature ranges with an interval of 50℃. The calculated results show that in Y–Ba–Cu–O system the complex oxides $BaCuO_2$ and Y_2BaCuO_5 are thermodynamically stable at roomtemperature (Fig. 2) and that $Y_2Cu_2O_5$ and

$YBa_2Cu_3O_{6.5}$ also become stable at temperatures higher than 300℃ and 750℃ respectively (Fig. 3 and Fig. 4). The phase transformation regularity shown by the calculated results agrees fairly well with the literatures [10,11].

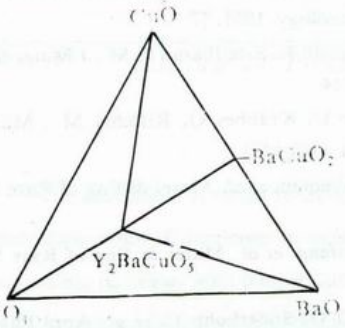

Fig.2 Calculated subsolidus phase relation diagram of the quasi-ternary system
$YO_{1.5}$–BaO–CuO in the temperature range of 25–250℃

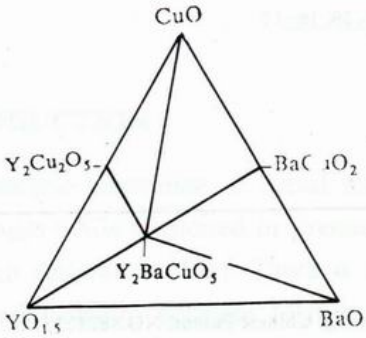

Fig. 3 Calculated subsolidus phase relation diagram of the quasi-ternary system
$YO_{1.5}$–BaO–CuO in the temperature range of 300–700℃

Although there might exist slight differences between the calculated diagrams and the experimental results at low temperature because the existence of some complex oxides which might appear at low temperature in the Y–Ba–Cu–O system have not been taken into account in the present work for lack of thermodynamic data thus far, however, the calculated subsolidus phase relation diagrams at high temperature agree with the experimental results fairly well. The calculated phase relations of $YO_{1.5}$–$BaCuO_2$–CuO in Fig.4 are completely the same as those determined by Hinks et al. [12] and the Philipps lab[13]. The calculated results of the present work show that the temperature must reach 750℃ or even higher for sintering and synthesizing the compound $YBa_2Cu_3O_{6.5}$ from the raw materials $YO_{1.5}$, BaO and CuO with their molar ratios being 1: 2: 3 in the quasi-ternary system $YO_{1.5}$–BaO–CuO. Therefore the sintering temperature should be as adequately high as possible for the preparation of single phase $YBa_2Cu_3O_{7-y}$ compound.

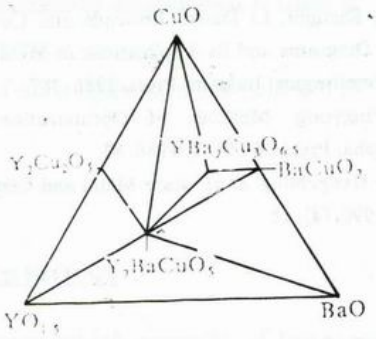

Fig. 4 Calculated subsolidus phase relation diagram of the quasi-ternary system
$YO_{1.5}$–BaO–CuO at a temperature higher than 750℃

5 CONCLUSIONS

In the research of high T_c superconductor oxide materials, the phase relation diagram is important for understanding the changes during the preparation process and for selecting its optimum conditions. However, it is difficult to construct a phase diagram experimentally, especially for the multicomponent phase diagram. Based on the thermodynamic theory and mathematical method, the principle and method for the calculation of subsolidus phase relation diagrams of the quasi-ternary system $YO_{1.5}$–BaO–CuO were developed. Using the thermodynamic data from authors' calorimetric experiments and other previous work, the subsolidus phase relation diagrams

of this system at various temperatures were calculated and constructed. From these phase diagrams, the relationship among the equilibrium phase in various temperature ranges can be dertermined clearly and it agrees fairly well with the experimental results. Therefore, our calculation method and the phase relation diagrams from this method are valuable for consultation and application, especially when experimental phase diagrams are not available.

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