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Solid State Equilibria in the Ba–Cu–O System

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Thermodynamic modeling is performed for the Ba–Cu–O system, which is essential to a good understanding of phase and chemical equilibria in the Y–Ba–Cu–O and some other oxide systems containing high-temperature superconductors. A self-consistent set of thermodynamic functions of the phases BaO_2, $BaCu_2O_2$, $BaCuO_2$, $Ba_2Cu_3O_{5+y}$, and Ba_2CuO_{3+q} is obtained. A variety of phase equilibria in the Ba–Cu–O system are calculated for a wide range of oxygen pressures and temperatures. The present thermodynamic data can be readily used for computing the phase equilibria and conditions for thermodynamic stability of oxide superconductors. It is detected that both $BaCuO_2$ and Ba_2CuO_{3+q} have two stability boundaries, one at low temperatures and high oxygen pressures, and the other at high temperatures and low oxygen pressures. Critical analysis of phase equilibria in the Ba–Cu–O system makes it possible to explain a number of conflicting results encountered in the literature. These contradictions arise from solid state reactions between phases, which may be very slow due to kinetic problems. © 1994 Academic Press, Inc.

INTRODUCTION

The system under consideration is a part of the quaternary Y–Ba–Cu–O system and the other oxide systems containing high-temperature superconductors. Conditions for thermodynamic stability of superconductors can be calculated based on thermodynamic properties of these phases and all the other phases that can occur in equilibrium with the superconductors. The phases $BaCu_2O_2$, $BaCuO_2$, and $Ba_2Cu_3O_{5+y}$ are often found in equilibria with the superconductors at low, medium, and high partial pressures of oxygen, respectively. That is why the Ba–Cu–O subsystem plays an important role in thermodynamics of high-temperature superconductors.

Considerable difficulties are encountered in experimental studies of this system because of high reactivity of Ba-rich phases, formation of $BaCO_3$ or carbonate-containing phases in air or oxygen of commercial grade, low cation mobility, and slow equilibration rate. Many phases have been reported in this system. Consistent notations will be used throughout to indicate the Ba : Cu ratio of the mixed oxide compounds. The phases $BaCuO_{2+x}$ (1 : 1), $BaCu_2O_2$ (1 : 2), $Ba_2Cu_3O_{5+y}$ (2 : 3), and Ba_2CuO_{3+q} (2 : 1) have been confirmed by a large number of authors (see e.g., Refs. (1–7)). A number of other compounds have also been reported, such as $BaCuO_{2.5}$, $BaCuO_{2.63}$ (8), $Ba_3Cu_5O_8$ (3), $BaCu_3O_4$ (9), and Ba_3CuO_4 (2, 5), but thermodynamic stability of these phases under some conditions remains unproved (a compound may be unstable, even though it has been synthesized as an almost single phase specimen).

Calculations of phase equilibria should be made taking into account only the phases established to be thermodynamically stable under some values of thermodynamic variables. At present these are BaO, BaO_2, CuO, Cu_2O, 1 : 2, 2 : 3, 1 : 1, and 2 : 1.

Here we critically review the thermodynamic properties of these phases and calculate the phase equilibria between them. At low temperatures or high oxygen pressures such equilibria can hardly be studied by a direct experiment while being essential to the understanding of a number of special features of these compounds. In this case thermodynamic calculations of the phase equilibria are feasible and valuable, because chemical thermodynamics is provided with powerful methods of estimation and extrapolation of thermodynamic functions to the range of variables where experimental data are lacking.

THERMODYNAMIC PROPERTIES

1. $BaCuO_{2+x}$

Although thermodynamic functions of the 1 : 1 phase have been reported in a lot of papers, they have not been established reliably yet. Enthalpies and entropies of the formation of this phase from oxides and oxygen are given in Table 1. Heats of the solution of 1 : 1 in acids were reported in Refs. (10–16), while Zhou and Navrotsky (17) used a lead borate glass as a solvent. The data in Refs. (18–21) were obtained by the emf method.

Some inconsistencies in the calorimetric measurements are apparent from Table 1 as well as a significant disparity between the calorimetric and emf data, which is greater than the errors of the measurements. A plausible explanation of these discrepancies and a relationship between thermodynamic properties and nonstoichiometry of the

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TABLE 1
Enthalpy and Entropy of the Reaction BaO + CuO + $(x/2)O_2 = BaCuO_{2+x}$

T(K)	x	$\Delta_r H$ (kJ/mole)	$\Delta_r S$ (J · mole^{-1}K^{-1})	Refs.
298.15	0	−98.2		(10)
298.15	0.05	−67.9[a]		(11)
298.15	0.095	−81.9[a]		(11)
298.15	0.00	−89.0 ± 6		(12)
298.15	0.02	−92.7 ± 6		(12)
298.15	0.05	−95.3 ± 6		(12)
298.15	0.06	−96.0 ± 6		(12)
298.15	0	−95.2 ± 8		(13)
325	0	−66 ± 6		(14)
298.15	0	−63.2		(15)
298	0.04	−62.9 ± 4.4		(16)
298.15	0.01	−85.2 ± 2.4		(17)
736–1102		−63.4	52.5	(18)
1101–1182	≈0	−40.1 ± 6.3	−5.6 ± 5.6	(19)
980–1160		−43.9	−7.3	(20)
1073–1223		−42.9	−7.8	(21)
298.15	0	−39.1	−4.1	Eq. [1]
1250	0	−40.2	−5.7	Eq. [1]

[a] Increased by 18.1 kJ/mol in response to correcting the heat of solution of $Cu(ClO_4) \cdot 6H_2O$ involved in a thermochemical cycle (see Ref. (12) for details).

1 : 1 phase are considered below in the discussion section. The authors have previously derived (22–25) the equation

$$\Delta_f G^{ox}(BaCuO_2)/R = -4669.0 - 0.261T - 0.132T(1 - \ln T) \quad [1]$$

for the Gibbs energy of the formation of 1 : 1 from oxides (BaO and CuO) and O_2 at $298 \leq T \leq 1250$ K, where R is the gas constant. This was derived from the Gibbs energy data of Skolis *et al.* (19) at 1100 K and the values of entropy and specific heat at 298 K estimated earlier (22–25). The way of this semiempirical estimation based on adding atomic contributions has been briefly described elsewhere (25). The entropy of formation calculated by Eq. [1] at 1100 K equals -5.5 J · mole^{-1} · K^{-1} in reasonable agreement with the data from Refs. (19–21) given in Table 1.

The investigation by Azad *et al.* (18) appears so different from the others that their results must be in error (see analysis of these data in Ref. (19)). The emf measurements of thermodynamic properties of the 1 : 1 phase are also reported by Idemoto *et al.* (26), who probably failed to identify properly the reaction corresponding to their galvanic cell. They reported the reaction

$$2BaCuO_{2+x} = BaCu_2O_2 + BaO + (x + 1/2)\,O_2,$$

but it seems that decomposition of CuO into Cu_2O and O_2 was in fact studied (see Fig. 6 in Ref. (26)).

2. *$Ba_2Cu_3O_{5+y}$*

This phase was first reported by Halász *et al.* (27) and studied in more detail by Thompson *et al.* (28). Most likely it has been just this phase which has been erroneously attributed to the formulas $BaCuO_{2.5}$ and $BaCuO_{2.63}$ (8), and $BaCuO_{2.35}$ (19) and $Ba_3Cu_5O_8$ (3). The errors in identification of the 2 : 3 phase result from the lack of direct control over the cation stoichiometry in most of the experiments. The other reason is that the single-phase 2 : 3 samples for the X-ray diffraction study can hardly be synthesized under normal conditions, i.e., without making use of lengthy periods of annealing or high oxygen pressures.

Williams *et al.* (29) reported direct measurements of the stoichiometry of phases by gravimetric and microprobe analysis. Mixtures of CuO and BaO_2 of the overall composition from 1 : 3 to 1 : 1 were reacted at 950°C for 40 hr in a 58-bar O_2 environment, and the phases CuO, $Ba_2Cu_3O_{5.96}$, $Ba_2Cu_3O_{5.84}$, $Ba_2Cu_{2.9}O_{5.84}$, $Ba_2Cu_{2.7}O_{5.26}$, $BaCuO_{2.43}$ were found, thus illustrating the difficulties associated with identification of the 1 : 1 and 2 : 3 phases.

A simple model for approximation of Gibbs energy of the 2 : 3 solid solution as a function of temperature and composition has been reported in our previous paper (25). The solid solution range for oxygen in $Ba_2Cu_3O_{5+y}$ is assumed to be $0 \leq y \leq 1$, so that $Ba_2Cu_3O_5$ and $Ba_2Cu_3O_6$ are end-member stoichiometric components of this solution. The entropy of the former was estimated earlier (25). The other parameters of the model were obtained from the data in Ref. (28). Use was made of four equations representing the equilibrium pressure of oxygen above the 2 : 3 phase at four temperatures and compositions reported by Thompson *et al.* (28). The conditions for equilibrium of the reaction $Ba_2Cu_3O_{5+y} = 2BaCuO_2 + CuO + (y/2)O_2$ in air at 1063 ± 10 K were also used (Thompson *et al.* (28) indicated that 2 : 3 was stable at 780°C and decomposed at 800°C). Equation [1] for the 1 : 1 phase was applied for the analysis of this equilibrium. The equations

$$\Delta_f H^{ox}(Ba_2Cu_3O_{5+y})/R = (1 - y)a_0 + ya_1 + y(1 - y)a_2, \quad [2]$$

$$\Delta_f S^{ox}(Ba_2Cu_3O_{5+y})/R = (1 - y)b_0 + yb_1 - y\ln y - (1 - y)\ln(1 - y), \quad [3]$$

were derived for the enthalpy and entropy of the formation of the 2 : 3 solid solution from BaO, CuO and O_2, where $a_0 = -5927.3$ K, $a_1 = -17196.7$ K, $a_2 = -8861.9$ K, $b_0 = -1.000$, and $b_1 = -10.079$. The condition of equilibrium between the 2 : 3 phase and the atmosphere is

$$\Delta\mu(O_2) = RT\ln P(O_2) = 2\Delta\mu(O) = 2[\partial\Delta_f G^{ox}(Ba_2Cu_3O_{5+y})/\partial y]_T.$$

Combining this equation with Eqs. [2] and [3] we arrive at the following relationship among the equilibrium pressures of oxygen, temperature, and composition of the 2 : 3 phase:

$$(T/2)\ln\{P(O_2), \mathrm{atm}\} = a_1 - a_0 + (b_0 - b_1)T + (1 - 2y)a_2 + T\ln[y/(1 - y)]. \quad [4]$$

Because of scarcity of the experimental data, Eqs. [2] to [4] are no more than a rough approximation. In particular, it does not reflect the existence of two different structures for the 2 : 3 phase suggested by Thompson *et al.* (28).

3. $BaCu_2O_2$

Here we used the thermodynamic properties of the 1 : 2 phase obtained in our earlier works (22–25). For the temperatures ranging between 298 and 1250 K, Gibbs energy of the reaction

$$BaO + Cu_2O = BaCu_2O_2 \quad [5]$$

was expressed as

$$\Delta_r G(T)/R = -5542.2 + 0.471T - 0.048T(1 - \ln T). \quad [6]$$

This equation was derived from the Gibbs energy at 1048 K measured by Pashin and Skolis (30), and from the entropy and specific heat estimated by adding together atomic contributions. The measurements of Pashin and Skolis (30) indicated that oxygen nonstoichiometry of the 1 : 2 phase is less than 0.02.

Idemoto *et al.* (26), when citing their earlier work (16), report the value of −695.4 ± 0.9 kJ/mol for the standard enthalpy of formation of 1 : 2 measured calorimetrically at 298 K. This yields 23.4 kJ for the enthalpy of reaction [5] as compared with −46.2 kJ calculated from Eq. [6]. In fact, the 1 : 2 phase is not mentioned in Ref. (16), and therefore it is impossible to find out the cause of such a significant discrepancy. It may be safely suggested that the original method of solution calorimetry applied in Ref. (16) was used to obtain the above-mentioned enthalpy of 1 : 2. It should be noted that the enthalpies of Idemoto *et al.* (16) are in poor agreement with the literature data. For example, the enthalpy of the formation of $YBa_2Cu_3O_{6.54}$ from oxides and oxygen was measured in Ref. (16) to be 3.2 ± 6.8 kJ/mol at 298 K. The same enthalpy reported by Zhou and Navrotsky (17) equals −80.1 ± 7.2 kJ/mol and agrees with several other investigations to within experimental error.

Idemoto *et al.* (26) also reported the decomposition of the 1 : 2 phase studied by the electromotive force method with zirconia electrolyte. Nevertheless, an analysis of their data leads us to the conclusion that decomposition of Cu_2O into Cu and O_2 was in fact studied.

Borowiec and Kolbrecka (21) expressed the Gibbs energy of reaction [5] over the range 1073–1223 K as $\Delta G_r(T)/R = -3651.3 + 0.108T$. Compared to Eq. [6], this yields far more positive values of ΔG_r. The cause of this discrepancy is unclear. A plausible explanation is that the measurements of Borowiec and Kolbrecka (21) were performed by the emf method with the electrode containing $BaCu_2O_2$ being in contact with the ZrO_2 electrolyte. Our thermodynamic calculations reveal that $BaCu_2O_2$ and ZrO_2 must react to form $BaZrO_3$ under these conditions, so that the equilibrium in the galvanic cell may be disturbed, and this may introduce large errors into the measurements (to exclude such a reaction, a thin layer of $Ce_{0.8}Gd_{0.2}O_{1.9}$ was applied on the surface of the zirconia electrolyte by Idemoto *et al.* (26), contrary to Borowiec and Kolbrecka (21)). In spite of this, the properties of $BaCuO_2$ obtained by the same method (21) are in reasonable agreement with the results of several other investigations, as can be seen in Table I.

4. Ba_2CuO_{3+q}

The oxygen nonstoichiometry of the 2 : 1 phase results from the formation of vacancies on an anion sublattice of the $-CuO_2-$ layer located in the basal plane (5, 31). A very similar plane is in the structure of the well-known superconductor $YBa_2Cu_3O_{6+z}$. The 2 : 1 phase is found in two structures, tetragonal and orthorhombic, in much the same way as $YBa_2Cu_3O_{6+z}$. If there were no vacancies in the basal plane, 2 : 1 would have the formula Ba_2CuO_4. But for the $YBa_2Cu_3O_{6+z}$ phase, half of sites on the anion sublattice in the basal plane are always vacant even at very high pressures of oxygen. The same is true for the 2 : 1 solid solution, and the oxygen content varies over the range $0 < q < 0.5$.

Zhang and Osamura (31) measured the temperature dependence of q at 0.21 atm of oxygen pressure. A drastic change in q from 0.32 to 0.09 was detected over the range 1033–1100 K, and the structural transformation from orthorhombic to tetragonal occurred at 1083 K. Since more detailed data on the function $q(T, P(O_2))$ are not available, as a first approximation, we put to use two stoichiometric compounds, tetragonal $Ba_2CuO_{3.1}$ and orthorhombic $Ba_2CuO_{3.3}$, to describe thermodynamic properties of the Ba_2CuO_{3+q} solid solution. This can be considered as a miscibility gap in the 2 : 1 phase, as is the case in $YBa_2Cu_3O_{6+z}$

at low temperatures (22, 32), when the solid solution decomposes into two phases.

Very few thermodynamic data are available for the 2 : 1 phase. Skolis *et al.* (33) measured Gibbs energy of the reaction

$$2BaO + CuO + (q/2)O_2 = Ba_2CuO_{3+q} \qquad [7]$$

at 969–1087 K by the emf method. The results obtained on different galvanic cells are in better agreement at high temperature; therefore, we used the value of the Gibbs energy at 1100 K and 1 atm of oxygen pressure that equals -50 ± 3 kJ/mol and presumably corresponds to formation of the orthorhombic phase. The entropies of the $Ba_2CuO_{3.1}$ and $Ba_2CuO_{3.3}$ compounds were estimated and combined with the above value of Gibbs energy and the orthorhombic-to-tetragonal transition point (31). The following equations were derived for the Gibbs energies of the formation of the compounds according to reaction [7]:

$$\Delta_f G^{ox}(Ba_2CuO_{3.1})/R = -9170 + 2.99T, \qquad [8]$$

$$\Delta_f G^{ox}(Ba_2CuO_{3.3})/R = -11689 + 5.16T. \qquad [9]$$

5. *BaO_2*

BaO and BaO_2 dissolve in each other in considerable quantities and form a continuous solid solution at $T \geq 1500$ K and $P(O_2) \geq 100$ atm. Unfortunately, the data that may permit the thermodynamic properties of this solution to be estimated are not available yet. Therefore, these phases were considered to be stoichiometric compounds at temperatures and oxygen pressures substantially lower than the critical values. Equilibrium conditions for the dissociation of BaO_2 were obtained by Aptekar' *et al.* (34). We used these data to derive the following equation for the Gibbs energy of the formation of BaO_2 from BaO and O_2 below 1323 K:

$$\Delta_f G^{ox}(BaO_2)/R = -8526 + 7.83T. \qquad [10]$$

CALCULATION OF PHASE EQUILIBRIA

As in our earlier works (22–25), phase equilibria were calculated by minimization of free energy or by evaluation of equilibrium conditions for all possible reactions between the phases in the Ba–Cu–O system. The above properties of phases, along with the thermodynamic functions of pure oxides presented in Ref. (25), were used for the calculations.

Several types of phase diagrams are of practical use, as exemplified in Figs. 1–4. An isothermal section of the temperature-composition phase diagram of the ternary $BaO–Cu_2O–O_2$ system is shown in Fig. 1. There are two independent composition variables on such a diagram. This type of diagram is useful for analysis of equilibria and processes in closed systems. For example, the sequence of equilibrium phase assemblages can easily be derived from the diagram if coulometric titration at fixed temperature is used to alter the oxygen content in the

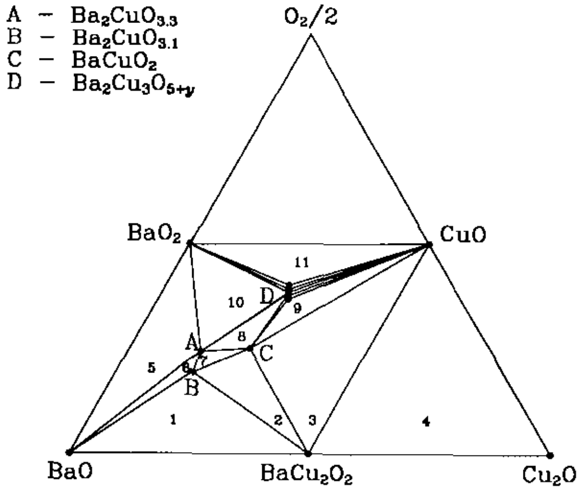

FIG. 1. Phase equilibria in the $BaO–Cu_2O–O_2$ system at 1100 K. Equilibrium pressures of oxygen in three-phase fields 1–11 are 1.46×10^{-7}, 4.09×10^{-5}, 7.21×10^{-3}, 2.32×10^{-3}, 1.17, 0.301, 0.301, 40.6, 0.350, 127, and 1.90×10^{5} atm, respectively.

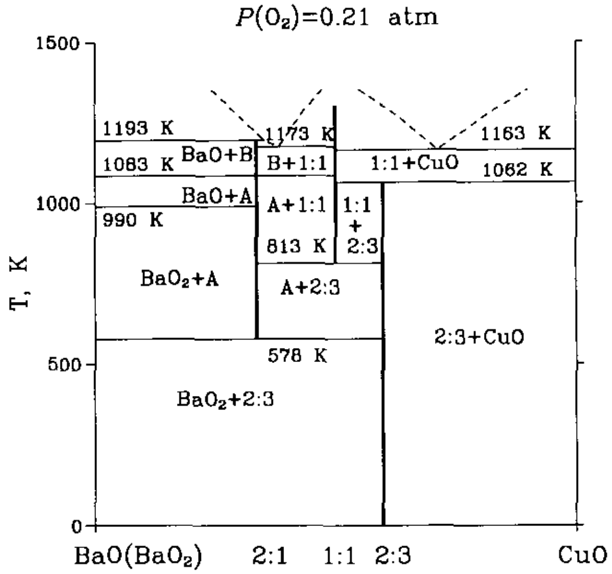

FIG. 2. Phase diagram of the system $BaO(BaO_2)–CuO$ at 0.21 atm of oxygen pressure. *A* and *B* denote the phases $Ba_2CuO_{3.3}$ and $Ba_2CuO_{3.1}$, respectively.

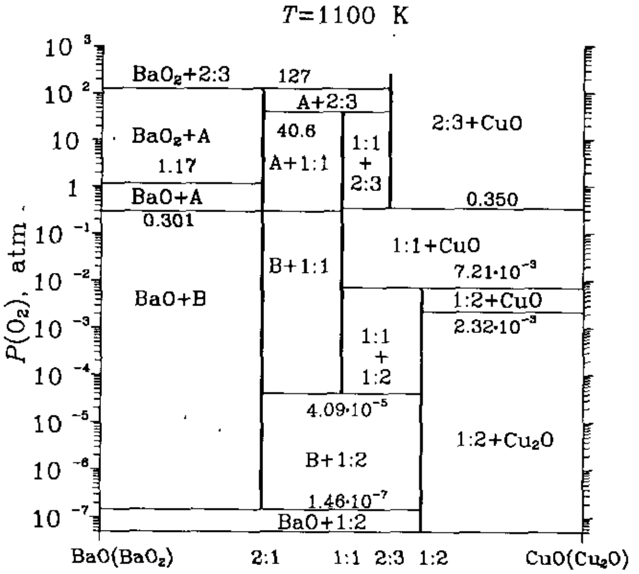

FIG. 3. Phase diagram of the system $BaO(BaO_2)$–$CuO(Cu_2O)$ at 1100 K. *A* and *B* denote the phases $Ba_2CuO_{3.3}$ and $Ba_2CuO_{3.1}$, respectively.

volume initially filled with specified quantities of BaO and CuO.

Examples of yet another type of phase diagram are shown in Figs. 2 and 3. These are plots of a potential function versus the composition, which is a molar metal ratio. One- and two-phase regions are indicated by vertical lines and areas, respectively. Horizontal lines represent univariant three-phase equilibria. A tentative liquidus is taken from Ref. (35). This type of diagram is useful to keep track of phase relations in the system, which is open with respect to oxygen, for example, when it is heated under fixed partial pressure of oxygen.

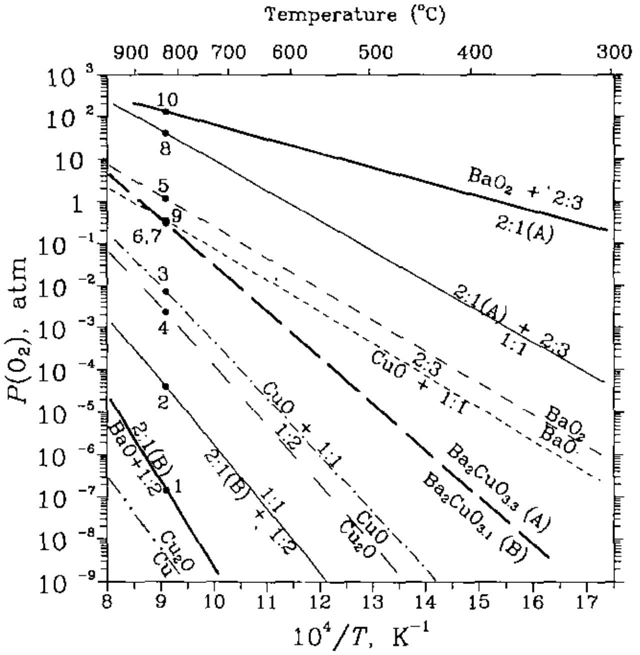

FIG. 4. Stability diagram of the Ba–Cu–O system. The curves correspond to univariant equilibria (11–20), which limits the stability ranges of the phases in this system. Points 1–10 correspond to the three-phase fields indicated in Fig. 1.

Another important type of phase diagram results when both axes are potential functions. This type is exemplified by the so-called stability (or predominance) diagram shown in Fig. 4. Stability fields of all the phases in the Ba–Cu–O system are superimposed over each other on this plot. Each line represents conditions for the corresponding two- or three-phase equilibrium, and the phases stable on each side of the line are indicated in Fig. 4. For example, the 2 : 1 phase is stable at temperatures and pressures between the bold solid lines, the 1 : 1 phase is stable between the thin solid lines, 2 : 3 is stable above the short dashed line, and the 1 : 2 phase is stable below the chained-dot line.

The stability fields of the phases in the Ba–Cu–O system are bounded by the reactions

$$2Cu_2O = 4Cu + O_2, \tag{11}$$

$$4CuO = 2Cu_2O + O_2, \tag{12}$$

$$2BaO_2 = 2BaO + O_2, \tag{13}$$

$$Ba_2CuO_{3.3} = Ba_2CuO_{3.1} + (0.1)O_2, \tag{14}$$

$$6Ba_2CuO_{3.3} + (3.1 + y)O_2 = 8BaO_2 + 2Ba_2Cu_3O_{5+y}, \tag{15}$$

$$2Ba_2CuO_{3.1} = 3BaO + BaCu_2O_2 + (0.6)O_2, \tag{16}$$

$$8BaCuO_2 + (0.3 + y)O_2 = 2Ba_2CuO_{3.3} + 2Ba_2Cu_3O_{5+y}, \tag{17}$$

$$3BaCuO_2 = Ba_2CuO_{3.1} + BaCu_2O_2 + (0.45)O_2, \tag{18}$$

$$Ba_2Cu_3O_{5+y} = CuO + 2BaCuO_2 + (y/2)O_2, \tag{19}$$

$$2BaCu_2O_2 + O_2 = 2CuO + 2BaCuO_2, \tag{20}$$

$$2BaCu_2O_2 = 2BaO + 4Cu + O_2, \tag{21}$$

$$2BaO = 2Ba + O_2, \tag{22}$$

$$2Ba_2Cu_3O_{5+y} + (2 - y)O_2 = 6CuO + 4BaO_2. \tag{23}$$

The equilibrium is reached in reactions [21] and [22] at very low, and in reaction [23] at very high oxygen pressures, so the corresponding lines fall outside the scale of Fig. 4. It is worth noting that the stability fields of all the phases may be limited by melting at high temperatures. Thermodynamic modeling of the liquid phase is outside the scope of the present study, and no attempts have been

TABLE 2

The Conditions for Equilibrium in Reactions [11–20] Approximated by the Equation $\log_{10}[P(O_2), \text{atm}] = A - B/T$

A	B	Reaction
7.4654	17450	[11]
10.0634	13972	[12]
6.8011	7405.6	[13]
9.4242	10941	[14]
5.1801	3379.9	[15]
11.9555	20665	[16]
8.1400	7172.1	[17]
9.3617	15121	[18]
6.4030	7530.9	[19]
9.9872	13330	[20]
8.2266	22378	[21][a]
10.5622	58022	[22][b]
5.4696	210.05	[23][c]

[a] Approximation over the range 825–1250 K.

[b] Approximation over the range 1050–1450 K.

[c] Approximation over the range 600–1250 K.

made to plot the lines related to formation of the liquid on Fig. 4.

The lines in Fig. 4 are approximated by linear equations, and the resulting coefficients are summarized in Table 2. Based on Fig. 4, the diagrams shown in Figs. 2 and 3 can readily be constructed for any oxygen pressure and temperature.

If the system BaO–Cu–O_2 is considered instead of BaO–Cu_2O–O_2, two additional three-phase regions appear in Fig. 1, namely, $BaCu_2O_2 + Cu_2O + Cu$ and $BaCu_2O_2 + BaO + Cu$. Equilibrium pressure of oxygen for these regions at 1100 K was calculated to be 4.00×10^{-9} and 7.66×10^{-13} atm, respectively. These are equilibrium conditions for reactions [11] and [21], respectively. The studies of the latter reaction have been reported in Refs. (21, 26, 36). The data in Refs. (21, 26) were discussed above, when thermodynamic properties of $BaCu_2O_2$ were considered. Golikov *et al.* (36) measured the pressure of oxygen above heterogeneous mixtures of $BaCu_2O_2$, BaO, and Cu. They obtained much higher values than those calculated in the present study; for example, $P(O_2) = 1.1 \times 10^{-10}$ atm was reported for the equilibrium of reaction [21] at 1100 K. Nevertheless, such pressures are too low to reach, in a reasonable amount of time, the equilibrium between the solid phases by exchange of oxygen through the gas phase. Hence, the experimental method employed by Golikov *et al.* (36) seems not to be reliable for the study of reaction [21].

DISCUSSION

The thermodynamic calculations reveal the main features of the phase equilibria in the Ba–Cu–O system. Nevertheless, the reality may be more sophisticated in some details, because a number of assumptions have been made in thermodynamic modeling of this system. First of all, we have to use simple thermodynamic models for some phases and neglect oxygen nonstoichiometry. No account has been taken of cation nonstoichiometry of the phases, because such data are lacking. It should be noted that the crystal structure of the 1 : 1 phase leaves room for a substantial solid solution range for metals in this phase (37). Our calculations take no account of the Ba_3CuO_4 phase that may exist at low oxygen pressures.

The uncertainty in thermodynamic functions of the phases may introduce errors into the calculated equilibrium temperatures and pressures, even though the qualitative description of phase equilibria is correct. For example, in Fig. 2 the temperatures of the three-phase equilibria involving the 1 : 2 and 2 : 3 phases may be several tens of K in error. Exact details of the thermodynamic properties and phase equilibria in this system must await further experimentation, but the results presented here can be helpful in setting the task of these experiments.

It should be noted that an unduly large error in the thermodynamic functions used for the calculations may lead to erroneous qualitative results. For example, Moiseev *et al.* (38) reported thermodynamic properties of 34 phases in the Y–Ba–Cu–O system calculated by empirical methods. Their enthalpies of formation of the 1 : 1 and 2 : 3 phases at 298 K are, respectively, 24 and 103 kJ/mole less than those derived here, while the entropies of the phases are similar. It can easily be shown that if the data from Ref. (38) were used for the calculations, the 1 : 1 phases would be thermodynamically unstable at any temperature and moderate oxygen pressure with respect to reaction [17], and would disappear from equilibrium phase diagrams. This is in conflict with the experimental evidence.

The conclusion to emerge from our thermodynamic calculations is that the 1 : 1 phase is unstable at low temperatures and high oxygen pressures. It must undergo decomposition reaction [17] at about 876 K in oxygen and at 813 K in air (see Fig. 2). The decomposition of the 1 : 1 phase upon cooling at 0.2–1 atm of oxygen pressure is also reported by Thompson *et al.* (28) and Roth (39). As can be seen in Fig. 2, the 2 : 1 phase also decomposes upon cooling, so that the ultimate products of the decomposition of the 1 : 1 phase at room temperature are BaO_2 and $Ba_2Cu_3O_{5+y}$. The presence of BaO_2 in the 1 : 1 samples has been reported in several papers; for example, the 1 : 1 samples for calorimetric measurements contained from 1 to 25 (!) mole% BaO_2 as indicated by X-ray diffraction

(11). However, there is no experimental evidence of the presence of $Ba_2Cu_3O_{5+y}$ in the 1 : 1 specimens. This may be due to the fact that the relatively new 2 : 3 phase has received little attention yet, or the crystallinity of the 2 : 3 precipitates is not enough to be detected by X-ray diffraction. At 90 atm of oxygen pressure, the decomposition of 1 : 1 into BaO_2 and 2 : 3 was detected below about 1000°C (7) as compared to 1116 K calculated in this study for the equilibrium of the reaction

$$3BaCuO_2 + [(1 + y)/2]O_2 = BaO_2 + Ba_2Cu_3O_{5+y}. \quad [24]$$

Some inconsistencies in calorimetric measurements of the enthalpy of the 1 : 1 phase and a significant disparity between the low-temperature calorimetric and high-temperature emf data (see Table 1) may be due to the partial decomposition of this phase. It should be noted that thermodynamic instability of a phase says nothing about how quickly it decomposes; and if a metastable equilibrium with a local minimum of free energy takes place, a specimen of the thermodynamically unstable phase may exist for an unlimited time under appropriate conditions. But in actual practice, such appropriate conditions are far from being obeyed at all times, so that the expectation of the slow kinetics of the decomposition is to be supported by the proper experiments.

In connection with the low-temperature instability of the 1 : 1 phase, we can take a fresh look at experimental data on the oxygen nonstoichiometry of this phase. Recently, Lindemer *et al.* (40) reported the results of a thorough study of the oxygen content in the 1 : 1 phase as a function of temperature and oxygen pressure by static thermogravimetry. The nonstoichiometry, x, in $BaCuO_{2+x}$ was measured (40) to range from 0 to 0.18 at 673–1223 K and oxygen pressure ranging between 10^{-4} and 1 atm, which is in reasonable agreement with several other investigations in oxygen. (The samples of this phase with $x < 0$ can be obtained by nonequilibrium annealing in inert gases (41).) Lindemer *et al.* (40) succeeded in detecting a number of distinctive features of this phase that were not observed in previous studies. These are breaks on the $x(T)$ isobars at some temperatures, which are clearly visible at low oxygen pressures, and the existence of two distinct curves $x(T)$ at $P(O_2) = 1$ atm and below about 1073 K.

We believe that these findings support the decomposition of the 1 : 1 phase, yet cast some doubt on the homogeneity range of this phase reported in Ref. (40) and in previous papers. Taking into account the oxygen nonstoichiometry of the 1 : 1 phase, reaction [17] can be written as

$$4BaCuO_{2+x} + [(0.3 + y - 4x)/2]O_2 = Ba_2CuO_{3.3} + Ba_2Cu_3O_{5+y}. \quad [25]$$

It can be obtained from Eq. [4] and x values reported in Ref. (40) that $(0.3 + y - 4x) > 0$. Hence, only the lower curve $x(P(O_2) = 1 \text{ atm}, T)$ and high-temperature parts of the other isobars in Ref. (40) can be attributed to the 1 : 1 phase, while the other data describe the properties of heterogeneous mixtures of the 1 : 1, 2 : 3, and 2 : 1 phases. There is no quantitative agreement between the data obtained by Lindemer *et al.* (40) and the overall calculated oxygen content in the phases on the righthand side of reaction [25], but this is to be expected, since only a small part of the 1 : 1 sample can decompose in reasonable time if reaction [25] does take place. This view is supported by the fact that 1 : 1 can exist for a long time at ambient conditions without any evidence of oxidation in air. The true value of the oxygen nonstoichiometry of the 1 : 1 phase is less than that which follows from the treatment of experimental data without regard for the partial decomposition of the samples. This is one of the reasons why the stoichiometric formula $BaCuO_2$ is used for the 1 : 1 phase in the present study.

Of importance in the emf measurements is the possibility of the formation of the 2 : 3 phase from 1 : 1 and CuO. As can be seen in Fig. 4, the equilibrium temperature for this reaction equals 1062 and 1181 K in air and 1 atm oxygen, respectively. Skolis *et al.* (19) measured the electromotive force on the galvanic cell $O_2|BaCuO_{2+x}$, CuO, $BaF_2|BaF_2|BaF_2$, CaO, $CaF_2|O_2$ and observed the drastic change of the temperature and oxygen pressure dependence of the emf, which may be attributed to reaction [19], that occurred in electrodes of the cell. If the 2 : 3 phase forms in the left electrode of the cell, the apparent value of x measured at 1100 K in 1 atm oxygen must be equal to about 0.3, taking into account that Eq. [4] gives $y \approx 0.6$ in $Ba_2Cu_3O_{5+y}$ under these conditions. Something like that value was actually obtained in Ref. (19).

In summary, a self-consistent set of thermodynamic functions of the phases in the Ba–Cu–O system has been derived from the critical analysis of all available data on the synthesis conditions of these phases, their structural features, thermodynamic properties, and phase equilibria. This makes it possible to calculate all kinds of phase equilibria between these phases.

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REFERENCES

1. R. S. Roth, K. L. Davis, and J. R. Dennis, *Adv. Ceram. Mater.* **2,** 303 (1987).
2. K. G. Frase, E. G. Liniger, and D. R. Clarke, *J. Am. Ceram. Soc.* **79,** C-204 (1987).
3. D. M. De Leeuw, C. A. H. A. Mutsaers, C. Langereis, H. C. A. Smoorenburg, and P. J. Rommers, *Physica C* **152,** 39 (1988).

4. R. S. Roth, C. J. Rawn, F. Beech, J. D. Whitler, and J. O. Anderson, *in* "Ceramic Superconductors II," (M. F. Yan, Ed.), p. 13. American Ceramic Society, Westerville, OH, 1988.
5. F. Abbattista, M. Vallino, C. Brisi, and M. Lucco-Borlera, *Mater. Res. Bull.* **23,** 1509 (1988).
6. F. Abbattista, M. Vallino, and D. Mazza, *Mater. Chem. Phys.* **21,** 521 (1989).
7. T. Graf, G. Triscone, A. Junod, and J. Muller, *J. Less-Common Met.* **170,** 359 (1991).
8. M. Arjomand and D. J. Machin, *J. Chem. Soc., Dalton Trans.* **11,** 1061 (1975).
9. A. Bertinotti, J. Hammann, D. Luzet, and E. Vincent, *Physica C* **160,** 227 (1989).
10. V. S. Grunin, M. M. Pivovarov, I. B. Patrina, M. V. Razumenko, R. A. Bubnova, M. I. Domina, and M. M. Shults, *Dokl. Akad. Nauk. SSSR* **307,** 143 (1989).
11. L. R. Morss, S. E. Dorris, T. B. Lindemer, and N. Naito, *Eur. J. Solid State Inorg. Chem.* **27,** 327 (1990).
12. A. S. Monaenkova, A. A. Popova, N. V. Zaitseva, M. A. Bykov, and S. L. Yaguzhinsky, *Sverkhprovodimost' Fiz. Khim. Tekh.* **3,** 955 (1990).
13. F. H. Garson, I. D. Raistrick, D. S. Ginley, and J. W. Halloran, *J. Mater. Res.* **6,** 885 (1991).
14. N. I. Matskevich, V. A. Titov, T. L. Popova, and V. P. Shaburova, "International Symposium on Calorimetry and Chemical Thermodynamics, Abstracts," p. 44. Moscow, 1991.
15. T. S. Kon'kova, Yu. N. Matyushin, Ya. Kh. Grinberg, and V. B. Lazarev, "13th All-Union Conference on Chemical Thermodynamics and Calorimetry, Abstract Pt. 1," p. 127. Krasnoyarsk, 1991.
16. Y. Idemoto, J. Takahashi, and K. Fueki, *Physica C* **194,** 177 (1992).
17. Z. Zhou and A. Navrotsky, *J. Mater. Res.* (1992), in press.
18. A. M. Azad, O. M. Sreedharan, and K. T. Jacob, "International Conference on High Temperature Superconductors, Abstracts," p. 530. Bangalore, India, 1990.
19. Yu. Ya. Skolis, S. F. Pashin, and M. L. Kovba, *Sverkhprovodimost' Fiz. Khim. Tekh.* **3,** 2792 (1990).
20. F. Zhanguo, J. Chunlin, and Z. Zhongxian, *J. Less-Common Met.* **161,** 49 (1990).
21. K. Borowiec and K. Kolbrecka, *J. Alloys and Compounds* **176,** 225 (1991).
22. G. F. Voronin, S. A. Degterov, and Yu. Ya. Skolis, "Proceedings, 3rd German–Soviet Bilateral Serminar on High-Temperature Superconductivity," p. 562. Karlsruhe, Germany, 1990.
23. S. A. Degterov and G. F. Voronin, *Physica C* **178,** 213 (1991).
24. G. F. Voronin, S. A. Degterov, and Yu. Ya. Skolis, *Dokl. Akad. Nauk. SSSR* **319,** 899 (1991).
25. G. F. Voronin, *Pure Appl. Chem.* **64,** 27 (1992).
26. Y. Idemoto, I. Ohyagi, and K. Fueki, *Physica C* **199,** 207 (1992).
27. I. Halász, I. Kirschner, T. Porjész, Gy. Kovács, T. Kármán, Gy. Zsolt, Cs. Sükösd, N. S. Rozlosnik, and J. Kürti, *Physica C* **153–155,** 379 (1988).
28. J. C. Thompson, J. D. F. Gerald, R. L. Withers, P. J. Barlow, and J. S. Anderson, *Mater. Res. Bull.* **24,** 505 (1989).
29. R. K. Williams, K. B. Alexander, J. Brynestad, T. J. Henson, D. M. Kroeger, T. B. Lindemer, G. C. Marsh, J. O. Scarbrough, and E. D. Specht, *J. Appl. Phys.* **70,** 906 (1991).
30. S. F. Pashin and Yu. Ya. Skolis, *Zh. Fiz. Khim.* **65,** 256 (1991).
31. W. Zhang and K. Osamura, *Jpn. J. Appl. Phys.* **29,** L1092 (1990).
32. G. F. Voronin and S. A. Degterov, *Physica C* **176,** 387 (1991).
33. Yu. Ya. Skolis, S. F. Pashin, S. V. Kitsenko, M. L. Kovba, and D. V. Fomichev, "13th All-Union Conference on Chemical Thermodynamics and Calorimetry, Abstracts, Pt. 1," p. 62. Krasnoyarsk, 1991.
34. I. L. Aptekar', A. V. Kosenko, A. A. Zhokhov, V. M. Masalov, and G. F. Emel'chenko, *Sverkhprovodimost' Fiz. Khim. Tekh.* **4,** 801 (1991).
35. W. Zhang, K. Osamura, and S. Ochiai, *J. Am. Ceram. Soc.* **73,** 1958 (1990).
36. Yu. V. Golikov, A. M. Yankin, I. N. Dubrovina, G. D. Deryabina, and V. F. Balakirev, *Sverkhprovodimost' Fiz. Khim. Tekh.* **4,** 2229 (1991).
37. E. F. Paulus, G. Miehe, H. Fuess, I. Yehia, and U. Löchner, *J. Solid State Chem.* **90,** 17 (1991).
38. G. K. Moiseev, N. A. Vatolin, S. I. Zaizeva, N. I. Ilyinych, D. S. Tsagareishvili, G. G. Gvelesiani, I. B. Baratashvili, and J. Šesták, *Thermochim. Acta* **198,** 267 (1992).
39. R. S. Roth, "User aspects of phase equilibria in high T_c ceramic superconductors"; in "Proceedings, User Aspects of Phase Equilibria," Joint Research Centre, Petten, Netherlands, June 25–27, 1990. Institute of Metals, London, 1990.
40. T. B. Lindemer, F. A. Washburn, and C. S. MacDougall, *Physica C* **196,** 390 (1992).
41. S. Eriksson, L.-G. Johansson, L. Börjesson, and M. Kakihana, *Physica C* **162–164,** 59 (1989).