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Phase equilibria in the Hg–Ba–Cu–O system

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Abstract

The already published data of temperatures and enthalpies of decomposition for mercury-based phases were combined with our experimental results from DSC and low-temperature calorimetry and the data for the Ba–Cu–O system taken from the literature. The consistent set of thermodynamic data of all phases in the Hg–Ba–Cu–O system was used for the calculation of the equilibrium phase composition under varying experimental conditions. The selected sections of the p_{O_2}–p_{Hg}–T stability phase diagram were constructed for the ratio of non-volatile components Ba:Cu = 2:1 and the temperatures of 500°C and 800°C. The decomposition temperatures of the Hg-1201 phase were calculated as a function of p_{O_2} for selected values of p_{Hg} as a parameter. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since the discovery of mercury-based high T_c superconductors in 1993 [1], the synthesis of these materials in the form of pure, single phase samples has been attended with a lot of difficulties due to their very low stability at elevated temperatures when the phase formation occurs. In order to avoid the mercury losses, the reaction must be carried out in sealed ampoules. However, under such conditions the experiments become highly irreproducible because of the variable partial pressures of mercury and oxygen (p_{Hg}, p_{O_2}) as well as total pressure being dependent on ampoule dimensions and applied temperature regime.

All high T_c superconducting mercury cuprates can be represented in a simplified way as a series $HgBa_2Ca_{n-1}Cu_nO_{2n+2}$. From the thermodynamic point of view the system Hg–Ba–Ca–Cu–O shares two components — mercury and oxygen — with the surrounding atmosphere. Consequently, the content of these components in the condensed phase, as well as the respective phase equilibria, can only be controlled by adjusting their activity, i.e., the composition of the surroundings. Indeed, some attempts have been made to control p_{O_2} by keeping an oxide redox couple (like Co_2O_3/CoO, CuO/Cu_2O [2] or

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Mn_2O_3/Mn_3O_4 [3]) at a given temperature in the same ampoule. The activity of mercury could be adjusted in a similar way, but it is obviously more difficult to find out the appropriate pair of Hg-compounds. Up to now the $HgBa_2CuO_4/Ba_2CuO_3$ couple has been tested for this purpose [2].

If we are able to control the experimental parameters mentioned above, the knowledge of the thermodynamic stability of relevant phases is of great importance for their synthesis. In this paper we have drawn our attention on the Hg–Ba–Cu–O system only containing the first member of the series — $HgBa_2CuO_4$, whose stability region in the p_{Hg}–p_{O2}–T space is studied by thermodynamic analysis followed by phase diagram calculations. The selected sections of this phase diagram which are of interest for the synthesis were calculated using the literature data for most frequently reported phases in the Ba–Cu–O system and the tabular data for simple oxides and gaseous Hg and O_2. The thermodynamic data for mercury containing mixed oxides were evaluated from the measured values of decomposition temperatures and enthalpies, and heat capacity data at low and high temperatures.

2. Experimental

The enthalpy of decomposition and the heat capacity measurement above room temperature were performed on the SETARAM HT-Multidetector calorimeter equipped with a heat flux DSC detector using the continuous heating regime (heating rate 5 K/min) in flowing oxygen atmosphere. The detector was calibrated on the NIST sapphire standard in powdered form and the calibration was tested by measuring the enthalpy of transformation of $BaCO_3$ at 802 K and by checking the concurrence of low- and high-temperature parts of heat capacity curve.

The low-temperature specific heat was measured in the range between 9 and 280 K by relaxation method. A plate-shaped sample was attached to Pt-resistance heater, which was connected by two tungsten wires to a heat sink equilibrated at desired temperature. When the sample is heated a temperature difference ΔT between the sample and the heat sink is stabilized at certain value and the stabilization rate is given by the characteristic value of relaxation time τ. Then the specific heat of the sample can be expressed as $C = P\tau/\Delta T$, where P is the heating power. The obtained value must be further corrected to an addenda dependent of the particular sample holder.

Only the barium mercurate $HgBaO_2$ was completely characterized by measuring its thermochemical properties in our laboratory. The enthalpy of formation $\Delta H_f°(298)$ of this substance was evaluated from the measured heat of decomposition into solid BaO and gaseous Hg and O_2. The reference value of entropy $S_m°(298)$ was calculated by integrating the determined low-temperature dependence of heat capacity over absolute temperature $(C_{pm}°(T)/T)$ in the temperature range from 0 to 298 K. The interval from 0 to 9 K was approximated by a cubic dependence. The Gibbs energy at a given temperature was calculated from the values of $\Delta H_f°(298)$ and $S_m°(298)$ using the measured high temperature dependence of specific heat (298–700 K).

The p_{Hg} vs. p_{O_2} decomposition line of Hg1201 superconductor was determined at 800°C by heating the sample in sealed ampoule at constant p_{O_2} (adjusted by Mn_2O_3/Mn_3O_4 mixture) and measuring the weight loss of the sample after quenching. The determined mass loss was used for the calculation of the equilibrium partial pressure of mercury, p_{Hg}.

The synthesis of $HgBaO_2$ and $HgBa_2CuO_4$ was carried out in sealed silica tubes by heating the mixture of appropriate amounts of metal oxides at 800°C for about 12 h. The partial pressure of oxygen during synthesis was controlled by Mn_2O_3/Mn_3O_4 getter placed in the same ampoule. All sample handling before the final heat treatment was carried out in a glovebox with an atmosphere depleted of moisture and CO_2. The phase purity of prepared materials was checked by powder XRD analysis (CuKα, DRON 3). Element composition was determined by EMA (JEOL Superprobe 733) operated at 20 kV and equipped with an energy dispersive X-ray spectrometer (EDX). The XPP correction supplied by Kevex was applied to the measured K-ratio.

3. Thermodynamic analysis

The thermodynamic analysis of the Ba–Cu–O subsystem is essential for precise description of the phase equilibria in the Hg–Ba–Cu–O system. Since Ba–Cu–O is a common subsystem to Y–Ba–Cu–O and some other oxide systems containing high T_c superconductors, it has been examined in detail by many authors [4–8] and a variety of phases have been reported. Unfortunately, due to a high reactivity of barium-rich compositions with atmospheric CO_2, some of them are considered to be actually oxycarbonates [9] and the thermochemical properties of others ($BaCuO_2$, Ba_2CuO_3, $BaCu_2O_2$) seem to be influenced by CO_2 dissolution [8]. The thermodynamic stability of phases Ba_3CuO_4, $BaCu_3O_4$ and $Ba_3Cu_5O_8$ remains still unproved [5]. From a multitude of original measured data and a number of assessments reported in literature for the Ba–Cu–O system, we chose the thermodynamic functions resulting from critical analysis published by Voronin and Degterov [5]. These functions represent a self-consistent set of data providing the equilibrium phase compositions, which are in accordance with experiment in a wide range of temperatures and partial oxygen pressures. The Ba_2CuO_{3+q} phase, which in fact shows a variable oxygen stoichiometry with a phase transition between tetragonal and othorhombic form, was simply considered to form two stoichiometric compounds, namely $Ba_2CuO_{3.1}$ and $Ba_2CuO_{3.3}$. The $Ba_2Cu_3O_{5+q}$ solid solution was modeled as a pseudobinary solution of $Ba_2Cu_3O_5$ and $Ba_2Cu_3O_6$ end members with one temperature independent regular solution parameter (73.70 kJ/mole). Let us note that the temperature dependence of the Gibbs energy of formation from oxides for the $BaCuO_2$ phase derived in the above mentioned assessment gives the lowest value of ΔH_{ox} ever reported. Nevertheless, we used this value in order to retain the self-consistency. For the $BaCu_2O_2$ phase the values of enthalpy and entropy of formation have been later confirmed by Lindemer and Schpecht [6].

The superconducting phase characterized by ideal formula $HgBa_2CuO_4$ (1201) shows in fact a variable stoichiometry of mercury and oxygen. A typical mercury deficiency found in our samples by measuring the weight loss after synthesis was about 0.1 Hg per formula unit, which was also confirmed by EMA. The formal copper valence $V_{Cu} = +2.20$ was determined using the empirical formula suggested in Ref. [12] after substituting a typical lattice parameter $a =$ 3.877 Å obtained from XRD. Assuming the formal valences $V_{Ba} = V_{Hg} = +2$, and $V_O = -2$ we obtain the ideal oxygen stoichiometry 4.0. Thus, the Hg1201 phase was considered to have a fixed stoichiometry $Hg_{0.9}Ba_2CuO_4$ and the deviation from this composition with respect to mercury and oxygen was neglected in our calculations. It should be noted that the mercury deficiency is very likely not realized by vacancies on Hg positions, but rather by a substitution of mercury by copper or carbonate group. However, considering that such a kind of substitution would make our model much more complex, it was neglected for our purposes.

The enthalpy of formation of the Hg1201 phase has been determined from heat of decomposition measured by DSC [10] ($\Delta H^\circ_{ox}(298) = -120 \pm 20$ kJ/mole), from the equilibrium condition of decomposition measured by a static weight technique [2] ($\Delta H^\circ_{ox}(298) \sim -61$ kJ/mole) and by TGA [11] ($\Delta H^\circ_{ox}(298) \sim -70$ kJ/mole), and recently from dissolution calorimetry [12] ($\Delta H^\circ_{ox}(298) = -102.0 \pm 3.3$ kJ/mole). The standard enthalpy of formation from oxides $\Delta H^\circ_{ox}(298) = -98.52$ kJ/mole used in our calculations is in quite good agreement with the results reported in Refs. [10,12], taking into account a different stoichiometry of oxygen and mercury in the phase studied. This value reproduces well the experimentally found conditions of the decomposition of Hg1201 into Ba_2CuO_{3+q}. On the contrary, the boundary decomposition line reported by Tsuchiya et al. [11] is shifted to higher p_{Hg}, which results in higher value of $\Delta H_{ox}{}^\circ(298)$. The value derived from the decomposition line determined by SWT [2] for 800°C is even higher, although the line is in good agreement with our results (see Fig. 3a). Its slope (0.266), however, is much smaller than one would expect from the Hg1201 stoichiometry. The standard entropy $S_m{}^\circ(298)$ of Hg1201 phase was taken from Ref. [10]. The temperature dependence of heat capacity was considered to obey the Neumann–Kopp rule.

The second mercury containing mixed oxide in the Hg–Ba–Cu–O system is the barium mercurate $HgBaO_2$ phase with a delafossite type structure. The calorimetric measurement of enthalpy of decomposition ($HgBaO_2$ (s) $\rightarrow$ BaO (s) + Hg (g) + $\frac{1}{2}$ O_2 (g)) provided a value of $\Delta H_r = 160$ kJ/mole. After recalculation to standard enthalpy of formation using the measured temperature dependence of heat capac-

Table 1
Employed values of standard molar enthalpy of formation from elements ($\Delta H_f°$) and from oxides ($\Delta H_{ox}°$), standard molar entropy ($S_m°$), entropy of formation from oxides ($\Delta S_{ox}°$), all at reference temperature of 298 K, and temperature dependence of standard molar heat capacity ($C_{pm}°$)

	$\Delta H_f°(298)$ [J/mole]	$\Delta H_{ox}°(298)$ [J/mole]	$S_m°(298)$ [J/mole K]	$\Delta S_{ox}°(298)$ [J/mole]	$C_{pm}° = a + bT + c/T^2 + dT^2 + e/T^3$ [J/mole K]				
					a	*b*	*c*	*d*	*e*
Ba_2Cu3O_5	−1613670	−49282	259.476	−8.314	236.584	5.44E−02	−2.74E+06	−1.36E−05	0
Ba_2Cu3O_6	−1707368	−142980	286.562	−83.801	251.161	5.77E−02	−2.84E+06	−1.41E−05	0
$Ba_2CuO_{3.1}$	−1328511	−76243	168.007	−24.86	140.852	3.99E−02	−1.23E+06	−1.36E−05	0
$Ba_2CuO_{3.3}$	−1349455	−97187	170.48	−42.902	143.767	4.05E−02	−1.25E+06	−1.38E−05	0
$BaCuO_2$	−743311	−39147	108.514	−4.09	92.897	2.35E−02	−9.92E+05	−6.80E−06	0
$BaCu_2O_2$	−783093	−64279	138.266	−24.1	120.268	2.08E−02	−1.81E+06	−2.57E−06	0
$HgBaO_2$	−680207	−41273	150.797	10.5	103.066	7.08E−02	−1.84E+06	0	0
$Hg_{0.9}Ba_2CuO_4$	−1435223	−98520	251	−5.1	232.698	7.47E−03	−7.04E+06	0	9.22E+08

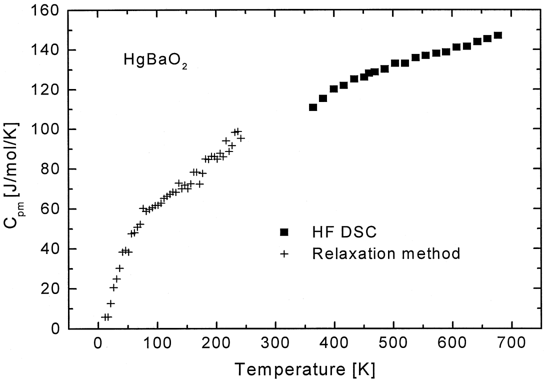

Fig. 1. Low- and high-temperature part of heat capacity of $HgBaO_2$ phase, measured by relaxation method and DSC, respectively.

ity (see Table 1 and Fig. 1) and reference data for oxides and gaseous Hg and O_2 we obtained $\Delta H_{ox}°(298) = -41.3$ kJ/mole. This value is about 22 kJ/mole higher than the recently published result of thermogravimetric study [13]. However, the value of $S_m°(298) = 138$ J/mole reported in the same paper is again lower than our value obtained from integration of low-temperature $C_{pm}°$ data ($S_m°(298) = 151$ J/mole), so that both differences in enthalpy and entropy compensate each other at higher temperatures in their effect on total Gibbs energy.

All thermodynamic data for binary and ternary mixed oxides used in the calculation are summarized in Table 1. SGTE [14] was employed as a source of data for metallic copper. The data for all simple oxides, as well as for gaseous mercury and oxygen, were taken from JANAF [15] and those for barium peroxide from Ref. [16].

4. Calculation

A general method [17] based on the minimization of the total Gibbs energy of the system on a set of points satisfying the material balance conditions was used for the calculation of equilibrium phase composition at given conditions. The minimization was performed under the constraints of fixed partial pressure (chemical potential) of oxygen and mercury in gaseous phase. Ideal behavior of the gas phase was considered ($a_i = p_i/p°$) and the formation of a liquid phase was not assumed in this work.

The phase diagrams were calculated by applying the following procedure. At first the individual points on the boundaries between the individual phase stability fields were searched by an iterative process when activities of free components and/or temperature were scanned and the equilibrium phase composition was detected. The corresponding boundary lines were subsequently calculated by integrating the Clapeyron-like equations:

$$\left(\frac{\partial T}{1/2\partial\ln p_{O_2}}\right)_{P,n_C,p_{Hg}} = -\frac{\Delta y_O RT_{eq}^2}{\Delta H - \Delta y_O H^\circ_{O_2}/2 - \Delta y_{Hg} H^\circ_{Hg}}, \tag{1}$$

$$\left(\frac{\partial T}{\partial\ln p_{Hg}}\right)_{P,n_C,p_{O_2}} = -\frac{\Delta y_{Hg} RT_{eq}^2}{\Delta H - \Delta y_O H^\circ_{O_2}/2 - \Delta y_{Hg} H^\circ_{Hg}}, \tag{2}$$

$$\left(\frac{\partial\ln p_{Hg}}{1/2\partial\ln p_{O_2}}\right)_{T,P,n_C} = -\frac{\Delta y_O}{\Delta y_{Hg}}, \tag{3}$$

where ΔH, Δy_{Hg} and Δy_{O_2} are, respectively, the differences of enthalpy, mercury content and oxygen content between the individual phase assemblages. The invariant points were found as intersections of boundary lines.

5. Results and discussion

The first type of the calculated predominance diagram is demonstrated on Fig. 2, where the stability fields in the Ba–Cu–O subsystem are shown as a function of temperature and oxygen pressure (p_{O_2}). These are the only two independent intensive variables in this subsystem. The ratio of non-volatile components was fixed to Ba:Cu = 2:1, so that all possible decomposition products of superconducting Hg1201 phase can be seen. Among them a relatively large stability field of the Ba_2CuO_{3+q} phase in its two structural forms spreads over the range of intermediate values of p_{O_2}. The regions of low- and high-partial pressures of oxygen are characterized by an occurrence of $BaCu_2O_2$ phase and $Ba_2Cu_3O_{5+q}$ solid solution, respectively.

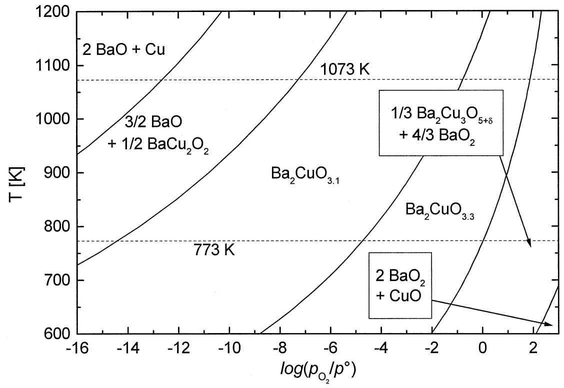

Fig. 2. Phase stability diagram (T vs. log p_{O_2}) of the Ba–Cu–O system calculated for the composition Ba/Cu = 1/2. Dashed lines indicate two temperature sections at which log p_{Hg} vs. log p_{O_2} were calculated.

The horizontal dashed lines in Fig. 2 indicate two temperatures, for which the isothermal cross-sections of T– p_{O_2}– p_{Hg} phase stability diagram of the Hg–Ba–Cu–O system were calculated. They were selected with respect to the potential applicability to adjust the appropriate conditions for synthesis and subsequent cooling of Hg1201 superconductor. At a typical synthesis temperature of 800°C (1073 K — see Fig. 3a) the stability field of Hg1201 phase is delimited by the regions of two polymorphs of Ba_2CuO_{3+q} at lower values of p_{Hg} and/or p_{O_2}. The different slope of $Ba_2CuO_{3.1}$ and $Ba_2CuO_{3.3}$ arises from the different oxygen content. As a matter of fact, the real oxygen stoichiometry in both phases varies gradually, so that the boundary lines would not be actually straight. At very high oxygen pressure ($p_{O_2} > 10^2$), Hg1201 decomposes into a mixture of $Ba_2Cu_3O_{5+\delta}$ and BaO_2. In this case the slope of boundary line is positive because of the higher oxygen content in $Ba_2Cu_3O_{5+\delta}/BaO_2$ compared to $Hg_{0.9}Ba_2CuO_4$. The upper bound (at high p_{Hg} and p_{O_2}) of the stability field of Hg1201 is formed by a couple $HgBaO_2$ and CuO. It is worth noting that the coexistence of these two fields is only feasible due to non-ideal stoichiometry of Hg1201 phase. If it were truly stoichiometric, then either $HgBaO_2$/CuO or $HgBa_2CuO_4$ would be stable.

If the temperature is lowered to 500°C (773 K) then all boundary lines of the Hg1201 stability field move down to lower values of p_{Hg} and p_{O_2} (see Fig. 3b). Consequently, the cooling of the sample from synthesis temperature must be carried out under simultaneous relief of mercury partial pressure in order to avoid the formation of $HgBaO_2$ and CuO. In comparison to $t = 800°C$, two additional regions appear in Fig. 3b, namely $HgBaO_2$ together with $Ba_2Cu_3O_{5+\delta}$ (around $p_{O_2} \sim 10^2$ and $p_{Hg} \sim 0.03$), and a three phase region $HgBaO_2$–CuO–HgO. However, the latter one is not a true stability region, since the boundary line can never be crossed going from the $HgBaO_2/CuO$ field. Instead, only solid HgO is formed and p_{Hg} and p_{O_2} are no more independently adjustable quantities. A similar effect occurs above the horizontal line at $p_{Hg} \sim 10$ where the condensation of liquid mercury takes place.

Fig. 4 shows the decomposition temperature of the $Hg_{0.9}Ba_2CuO_4$ phase to Ba_2CuO_{3+q} or $Ba_2Cu_3O_{5+\delta}/BaO_2$ mixture as a function of oxygen pressure for selected values of mercury pressure. This information is of practical use for the control of partial pressure of mercury during synthesis of Hg-based superconductors by heating a couple Hg1201/Ba_2CuO_{3+q} at given temperature. It can also help for the estimation of critical synthesis and annealing conditions, which should not be passed over to avoid decomposition.

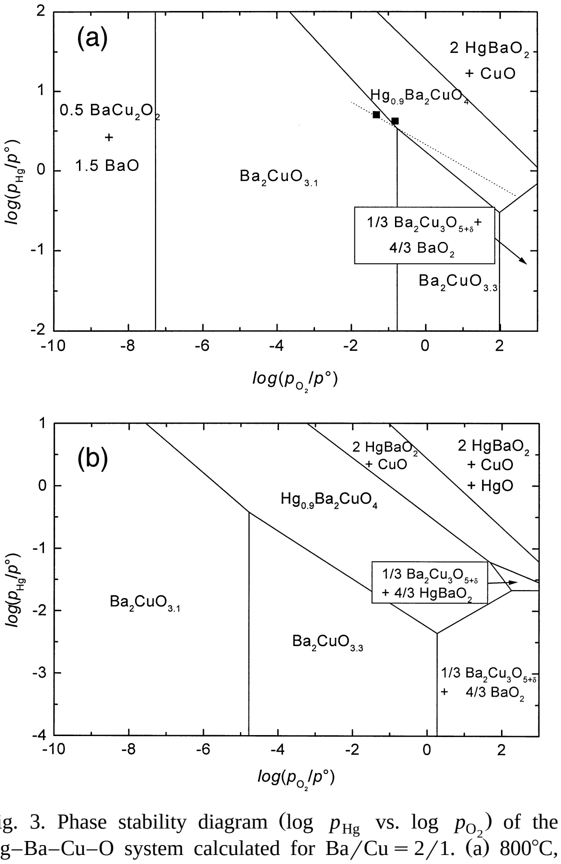

Fig. 3. Phase stability diagram (log p_{Hg} vs. log p_{O_2}) of the Hg–Ba–Cu–O system calculated for Ba/Cu = 2/1. (a) 800°C, (b) 500°C. ■ — our results; … Alyoshin et al. [2].

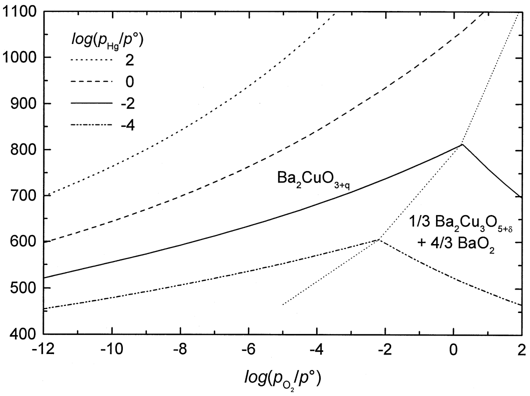

Fig. 4. Decomposition temperature of the superconducting phase $Hg_{0.9}Ba_2CuO_4$ as a function of log p_{O_2} for some selected values of log p_{Hg}.

6. Conclusion

Phase stability diagrams log p_{O2}–T in the Ba–Cu–O subsystem and log p_{O2}–log p_{Hg} at $t = 500°C$ and $t = 800°C$ in the Hg–Ba–Cu–O system were calculated for the compositions of stable components: Ba/Cu = 2/1.

Superconducting cuprate $Hg_{0.9}Ba_2CuO_4$ was found to be stable within a relatively large stability field at both studied temperatures.

At lower p_{Hg} phases decomposes into Ba_2CuO_{3+x} within a wide range of p_{O_2}. At higher p_{O_2} the phase $Ba_2Cu_3O_{5+x}$ is contained in the decomposition product, while at lower p_{O_2} the phase $BaCu_2O_2$ is formed.

At higher p_{Hg} the barium mercurate $HgBaO_2$ is stable in the mixture with CuO.

Acknowledgements

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