

The Oxygen Potentials Corresponding to the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ Phase in the Y-Ba-Cu-O System

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Phase relations in the vicinity of the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ in the CuO-rich part of the Y-Ba-Cu-O system were studied by the equilibration and quenching technique. At 950°C, the system is characterized by the large number of solid four-phase combinations. The oxygen potential as a function of temperature for two four-phase combinations, i.e., $\text{YBa}_2\text{Cu}_3\text{O}_{6+x} + \text{BaCuO}_2 + \text{BaCu}_2\text{O}_2 + \text{Y}_2\text{BaCuO}_5$ and $\text{YBa}_2\text{Cu}_3\text{O}_{6+x} + \text{BaCu}_2\text{O}_2 + \text{Y}_2\text{BaCuO}_5 + \text{Cu}_2\text{O}$, were studied by means of solid state EMF measurements. At higher oxygen potentials the pair of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ and Y_2BaCuO_5 is stable in contact with BaCuO_2 . At lower oxygen pressures this pair coexists in equilibrium with BaCu_2O_2 or Cu_2O . © 1991 Academic Press, Inc.

Introduction

Since the discovery of superconductivity at about 90K in the system Y-Ba-Cu-O by Chu *et al.* (1) and the identification of the superconducting compound $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ by Cava *et al.* (2), designated as Y_{123} , the system has been investigated very intensively, and a large number of measurements have been carried out on the Y_{123} phase. The interpretation of many of such measurements, however, depends on a presence of the secondary phases, i.e., minor amounts of reactants or the binary oxides from the Y-Ba-Cu-O system. It is clear that the information on the phase relations around the superconducting phase is urgently necessary for preparing superconducting materials by solid-state sintering or liquid-phase solidification. The future applications of Y_{123} will depend partly on its thermodynamic stability over the range of

temperatures and the oxygen pressures to which the superconductor is exposed during its fabrication and use.

The first proposal for a phase diagram around the superconducting phase in the BaO- Y_2O_3 -CuO system in air was made by Hwu *et al.* (3). They found that at 950°C Y_{123} coexists in equilibrium with Y_2BaCuO_5 (Y_{211}), BaCuO_2 , and CuO. The semiconducting compound Y_2BaCuO_5 was first described by Michel and Raveau (4).

Frase *et al.* (5) have reported the BaO- Y_2O_3 -CuO system at 950°C with three ternary cuprates, i.e., $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ (Y_{123}), Y_2BaCuO_5 (Y_{211}), and $\text{YBa}_3\text{Cu}_2\text{O}_{6.5+x}$ (Y_{132}). The authors have stated the coexistence of the Y_{132} with Y_{211} , Y_2BaO_4 , $\text{Y}_2\text{Ba}_4\text{O}_7$, and BaCuO_2 in air at 950°C. The ternary cuprate $\text{YBa}_3\text{Cu}_2\text{O}_{6.5+x}$, which was first described by Roth *et al.* (6), appears in two versions, one "ordered" tetragonal and one "disordered" cubic obtained by the quenching of

partially molten mixtures. Instead of $\text{YBa}_3\text{Cu}_2\text{O}_{6.5+x}$, Fjellvag *et al.* (7) have found $\text{YBa}_8\text{Cu}_4\text{O}_{12+n}$ in coexistence with Y_2BaCuO_5 , BaCuO_2 , and BaO_2 . De Leeuw *et al.* (8) have presented a $\text{BaO}-\text{Y}_2\text{O}_3-\text{CuO}$ phase diagram in air at 950°C with five ternary cuprates; in addition to $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ and Y_2BaCuO_5 , three new cuprates were found, namely, $\text{YBa}_4\text{Cu}_3\text{O}_{8.5+x}$ (Y_{143}), $\text{Y}_3\text{Ba}_8\text{Cu}_5\text{O}_{17.5+x}$ (Y_{385}), and $\text{YBa}_5\text{Cu}_2\text{O}_{8.5+x}$ (Y_{152}).

Recently, Reichelt *et al.* (9) have found the existence of $\text{Y}_2\text{Ba}_5\text{Cu}_3\text{O}_x$ (Y_{253}) instead of Y_{143} and Y_{385} in air at 900°C . They have shown the coexistence of Y_{253} with Y_{211} , Y_{152} , BaCuO_2 , Ba_2CuO_3 , $\text{Y}_2\text{Ba}_4\text{O}_7$, and $\text{Y}_2\text{Ba}_2\text{O}_5$.

The present study of the equilibrium phase relationships around Y_{123} has been carried out for variable oxygen potentials at 950°C . The majority of the starting mixtures were located in a CuO -rich part of the $\text{Y}-\text{Ba}-\text{Cu}-\text{O}$ system. The oxygen potentials, being only a function of phase combination and temperature, were obtained for the chosen stable four-phase combination by EMF measurements using a $\text{ZrO}_2(\text{CaO})$ solid electrolyte with pure oxygen as the reference electrode and with the sample protected by an atmosphere of purified argon.

The quaternary system $\text{Y}-\text{Ba}-\text{Cu}-\text{O}$ may conveniently be illustrated by a tetrahedron, Fig. 1. In the diagram the four oxides Y_2O_3 , BaO , CuO , and Cu_2O are chosen as the components, and represent the four corners in a tetrahedron. The stable binary oxides at 950°C are indicated on the edges. According to the phase rule the sum $P + F$ (phases + degrees of freedom) for a quaternary system is six. At a fixed temperature and in air the maximum number of phases is four, which may be three solids and the gas phase, each of a fixed composition. Inside the $\text{CuO}-\text{BaO}-\text{Y}_2\text{O}_3-\text{Cu}_2\text{O}$ tetrahedron and for a variable oxygen potential the maximum number of coexisting

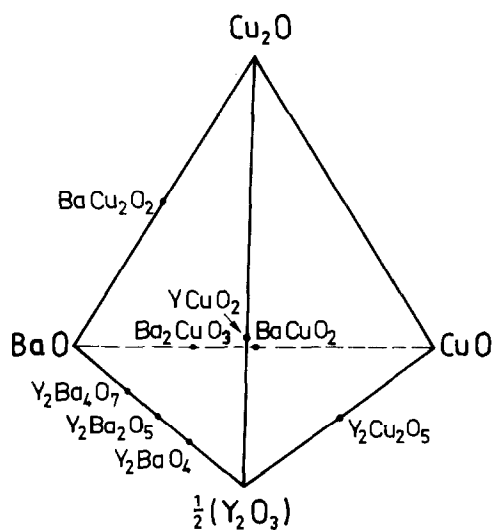
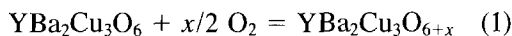


FIG. 1. The $\text{BaO}-\text{Y}_2\text{O}_3-\text{CuO}-\text{Cu}_2\text{O}$ tetrahedron with the binary oxides on the edges.

solid phases is four and the composition of all four phases is fixed for a given temperature.

The previously used two steps of experimental procedure (10) based on firing in air the powders of BaCO_3 , CuO , and Y_2O_3 and then mixing the resulting three-phase combination with Cu_2O and annealing in evacuated and sealed silica tubes has led to the nonequilibrium four-phase combination and then to incorrect EMF values. Disregarding the slight contamination of specimens with silica during heat treatment at 950°C , the main reason for obtaining a nonequilibrium mixture is the oxidation of Cu_2O by $\text{YBa}_2\text{Cu}_3\text{O}_7$ or other ternary cuprates in the evacuated silica tubes.

It is well known that, during cooling in air, the oxygen is continuously taken up by the semiconducting phase Y_{123} with an increasing $\text{Cu}^{+3}/\text{Cu}^{+2}$ ratio. The semiconductor $\text{YBa}_2\text{Cu}_3\text{O}_6$ is transformed during oxidation from high temperature tetragonal to the low temperature orthorhombic superconducting phase according to the reaction;



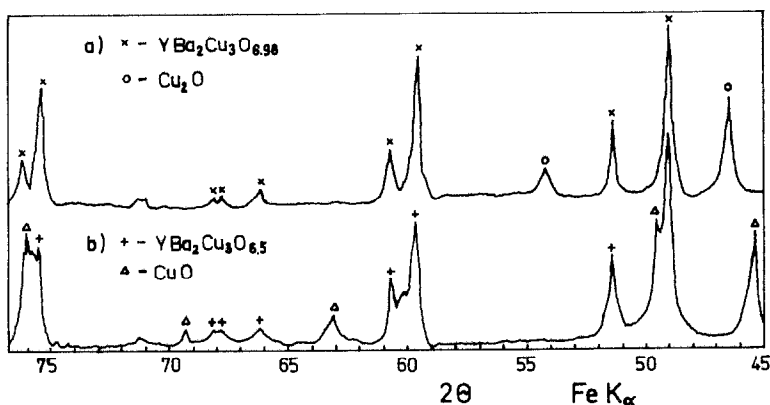
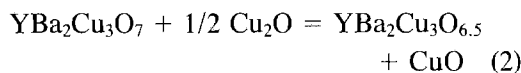


FIG. 2. The X-ray diffraction patterns of the starting mixture (a) and (b) after annealing in evacuated and sealed silica tubes at 950°C.

The oxidized form of Y_{123} with the composition close to the $YBa_2Cu_3O_7$ can act as an oxidation agent for the added Cu_2O via the following reaction;



We have investigated Reaction (2) by mixing stoichiometric amounts of the previously obtained $YBa_2Cu_3O_{6.98}$ with Cu_2O and annealing in the evacuated and sealed silica tube at 950°C for 24 hr. The X-ray patterns presented in Fig. 2 show that the starting mixture, i.e., $YBa_2Cu_3O_{6.98}$ and Cu_2O , was converted completely to the less oxidized form of Y_{123} , i.e., $YBa_2Cu_3O_{6.5}$ and CuO . Thus, the simple mixing of the slowly cooled in air three-phase combination which contains of the fully oxidized form of the Y_{123} with Cu_2O will lead after annealing to the formation of CuO . Depending on the amounts of Cu_2O added the resulting mixture will contain a four-phase combination, i.e., CuO instead of Cu_2O or a nonequilibrium five-phase mixture. The EMF measurements on such samples gave the oxygen potential values close to the Cu_2/CuO equilibrium (10, 11).

The next experimental procedure (12) was introduced in order to avoid the oxida-

tion of Cu_2O . In this case the mixtures of $BaCO_3$, CuO , and Y_2O_3 after firing in air, i.e., the resulting three-phase combinations prior to mixing with Cu_2O , were cooled or quenched in nitrogen. However, this procedure does not guarantee the equilibrium phase combination due to the fact that the given three-phase combination can coexist with one of the phases Cu_2O , $BaCu_2O_2$, and $YCuO_2$, which are located on the upper corner and on the edges of the tetrahedron in Fig. 1.

This problem can be solved by producing in one step the equilibrium four-phase combination. In this work the experimental procedure which gave directly the four-phase combination based on the reaction between $Y_2Ba_4O_7$, CuO , and Cu or $Y_2Cu_2O_5$, $BaCuO_2$, and Cu has been used.

Experimental

The samples with the composition situated in the CuO -rich part of the CuO - BaO - Y_2O_3 - Cu_2O tetrahedron were obtained by a solid-state reaction of the compressed powders of $Y_2Ba_4O_7$, CuO , and Cu or $BaCuO_2$, $Y_2Cu_2O_5$, and Cu in the evacuated and sealed silica tubes at 950°C. The binary oxides, i.e., $Y_2Ba_4O_7$, $BaCuO_2$, and $Y_2Cu_2O_5$

were prepared by high temperature synthesis in air at 950°C from the calculated amounts of the necessary chemicals: $\text{Y}_2\text{Ba}_4\text{O}_7$ was made from Y_2O_3 and BaCO_3 , BaCuO_2 from CuO and BaCO_3 , $\text{Y}_2\text{Cu}_2\text{O}_5$ from Y_2O_3 and CuO . Accurately calculated and weighed amounts of $\text{Y}_2\text{Ba}_4\text{O}_7$, CuO , and Cu or BaCuO_2 , $\text{Y}_2\text{Cu}_2\text{O}_5$, and Cu were ground thoroughly together in a mortar under absolute alcohol and dried. In order to exclude any chemical reaction between the silica tube and the starting mixture, the samples were first placed in small test tubes of alumina and compressed by ramming with an iron rod. These test tubes were placed inside the silica tubes which were evacuated and sealed and then were annealed at 950°C until X-ray diffraction analysis of the quenched samples showed that a stable four-phase combination was established. In general, 3–6 days of annealing were needed. This procedure gave a fast reaction due to intimate contact between the different particles.

For EMF measurements 0.5–1.0 g of the powdered mixture which represented the chosen four-phase combination was placed inside the $\text{ZrO}_2(\text{CaO})$ tube, together with a platinum lead pressed against the bottom of the tube, Fig. 3. The tube communicated with a slow flow of argon which maintained a total gas pressure of 1 atm inside the tube. The reference electrode was a piece of platinum gauze pressed against the outside bottom of the tube, and was flushed with a slow flow of oxygen of atmospheric pressure. A platinum lead, which also served as one leg of a Pt–Pt/Rh thermocouple was welded to the gauze. The EMF values were measured at temperature intervals of $20\text{--}30^\circ\text{C}$ in the range $750\text{--}1000^\circ\text{C}$ and measurements were started at about 950°C and were made repeatedly at decreasing and increasing temperatures. Above 980°C the EMF values became scattered due to a partial melting of the working electrode. The oxygen potential p_{O_2} inside the reaction mixture

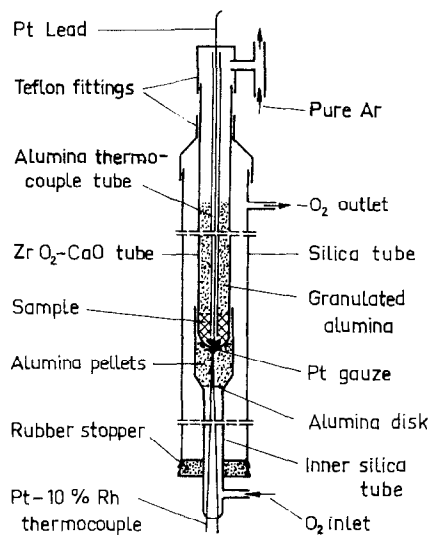


FIG. 3. EMF cell. The cell is surrounded by a grounded shield and is mounted inside a tube furnace.

is related to the EMF, E , to the temperature, T , and to the oxygen potential of the reference electrode $p_{\text{O}_2}^\circ$ by the Nernst equation:

$$\log p_{\text{O}_2} (\text{atm}) = \frac{4FE}{2.303RT} + \log p_{\text{O}_2}^\circ, \quad (3)$$

where R is the gas constant and F is the Faraday constant.

Results

The various phase combinations which were obtained by annealing in evacuated and sealed silica tubes and observed by X-ray diffraction are listed in Table I. As previously mentioned, two types of starting mixture, namely $\text{Y}_2\text{Ba}_4\text{O}_7 + \text{CuO} + \text{Cu}$ and $\text{Y}_2\text{Cu}_2\text{O}_5 + \text{BaCuO}_2 + \text{Cu}$, were used for annealing. In addition to the resulting equilibrium combinations the table gives also the composition of the starting mixtures. Figure 4 gives the phase relation in the CuO -rich part of the CuO – BaO – Y_2O_3 – Cu_2O phase diagram at 950°C as deduced from the X-ray work for the six four-phase

TABLE I
 SAMPLES ANNEALED FOR 3–6 DAYS AT 950°C AND QUENCHED. ALL CONCENTRATIONS ARE
 IN MOLE PERCENT

No.	$N_{Y_2Ba_4O_7}$	N_{CuO}	N_{Cu}	$N_{Y_2Cu_2O_5}$	N_{BaCuO_2}	Phases present
1	0.143	0.714	0.143	—	—	Y_{123}
2	—	—	—	0.200	0.800	Y_{123}
3	—	—	—	0.800	0.200	$Y_2Cu_2O_5 + Y_{211} + CuO$
4	—	—	0.222	0.222	0.556	$Y_{123} + Y_{211} + CuO + Cu_2O$
5	0.118	0.588	0.294	—	—	$Y_{123} + Y_{211} + BaCu_2O_2 + Cu_2O$
6	—	—	0.333	0.333	0.333	$Y_{211} + CuO + Cu_2O$
7	—	—	0.250	0.500	0.250	$Y_{211} + Y_2Cu_2O_5 + CuO + Cu_2O$
8	—	—	0.571	0.286	0.143	$Y_{211} + YCuO_2 + Cu_2O$
9	—	—	0.500	0.375	0.125	$Y_{211} + Y_2Cu_2O_5 + YCuO_2 + Cu_2O$
10	0.154	0.692	0.154	—	—	$Y_{123} + Y_{211} + BaCuO_2 + BaCu_2O_2$
11	0.143	0.643	0.214	—	—	$Y_{123} + Y_{211} + BaCuO_2 + BaCu_2O_2$
12	—	—	0.300	0.100	0.600	$Y_{123} + BaCuO_2 + BaCu_2O_2 + Cu_2O$
13	—	—	0.334	0.083	0.583	$Y_{123} + BaCuO_2 + BaCu_2O_2 + Cu_2O$
14	—	—	0.250	0.125	0.625	$Y_{123} + BaCuO_2 + Cu_2O$

Note. $Y_{123} = YBa_2Cu_3O_{6+x}$ ($x = 0.02$); $Y_{211} = Y_2BaCuO_5$.

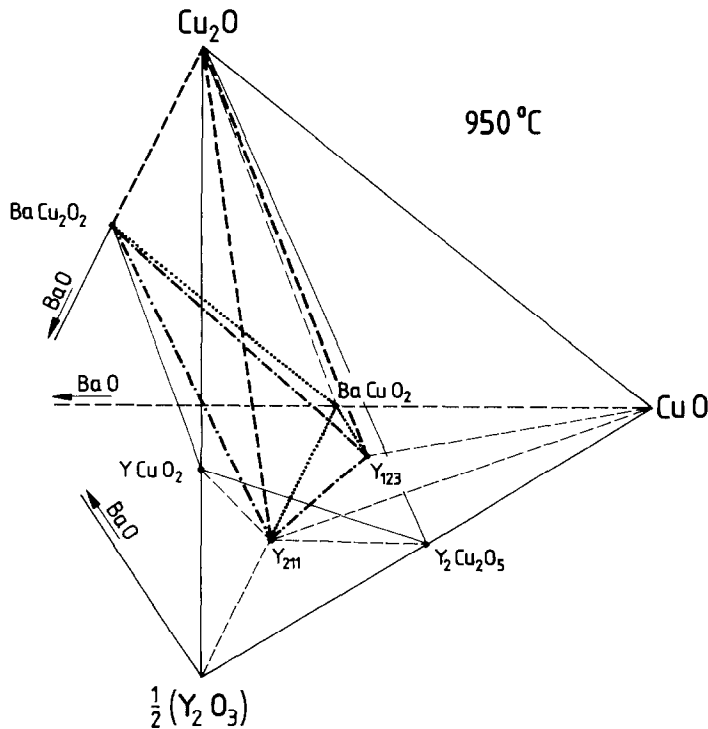


FIG. 4. The system BaO – Y_2O_3 – CuO – Cu_2O around the $YBa_2Cu_3O_{6+x}$ at 950°C. The presence of a liquid phase close to the $BaCuO_2$ – CuO tie-line has been disregarded. The oxygen potential has been measured for tetrahedrons with dashed, thick lines.

combinations and for the four three-phase combinations. For simplification, the formation of the liquid in the $\text{BaCuO}_2\text{-Y}_{123}\text{-CuO-Cu}_2\text{O}$ subtetrahedron close to the $\text{BaCuO}_2\text{-CuO}$ tie-line has been omitted. From the stability point of view this four-phase combination is less interesting. The oxygen potential within this subtetrahedron is given by $\text{Cu}_2\text{O/CuO}$ equilibrium. No equilibrating experiments were carried out on this part of the system. Experimental procedures used in the previous work (10, 12) gave the incorrect sequence of the four-phase combination around Y_{123} . Generally speaking, two binary compounds, i.e., BaCu_2O_2 and YCuO_2 , have not been found in the equilibrium with ternary cuprates in the investigated part of the diagram.

The present work shows that this part of the system is characterized by the following four-phase regions:

1. $\text{YBa}_2\text{Cu}_3\text{O}_{6+x} + \text{BaCuO}_2 + \text{BaCu}_2\text{O}_2 + \text{Cu}_2\text{O}$
2. $\text{YBa}_2\text{Cu}_3\text{O}_{6+x} + \text{BaCuO}_2 + \text{BaCu}_2\text{O}_2 + \text{Y}_2\text{BaCuO}_5$
3. $\text{YBa}_2\text{Cu}_3\text{O}_{6+x} + \text{BaCu}_2\text{O}_2 + \text{Cu}_2\text{O} + \text{Y}_2\text{BaCuO}_5$
4. $\text{YBa}_2\text{Cu}_3\text{O}_{6+x} + \text{Y}_2\text{BaCuO}_5 + \text{CuO} + \text{Cu}_2\text{O}$
5. $\text{Y}_2\text{BaCuO}_5 + \text{Y}_2\text{Cu}_2\text{O}_5 + \text{CuO} + \text{Cu}_2\text{O}$
6. $\text{Y}_2\text{BaCuO}_5 + \text{Y}_2\text{Cu}_2\text{O}_5 + \text{Cu}_2\text{O} + \text{YCuO}_2$

Besides these four-phase combinations the following three-phase regions were found:

7. $\text{YBa}_2\text{Cu}_3\text{O}_{6+x} + \text{BaCuO}_2 + \text{Cu}_2\text{O}$
8. $\text{Y}_2\text{BaCuO}_5 + \text{CuO} + \text{Cu}_2\text{O}$
9. $\text{Y}_2\text{BaCuO}_5 + \text{Y}_2\text{Cu}_2\text{O}_5 + \text{Cu}_2\text{O}$
10. $\text{Y}_2\text{BaCuO}_5 + \text{YCuO}_2 + \text{Cu}_2\text{O}$

On the basis of these experimental data it was possible to predict additional four-phase combinations:

11. $\text{YBa}_2\text{Cu}_3\text{O}_{6+x} + \text{BaCuO}_2 + \text{CuO} + \text{Cu}_2\text{O}$

12. $\text{Y}_2\text{BaCuO}_5 + \text{Y}_2\text{Cu}_2\text{O}_5 + \text{YCuO}_2 + \text{Y}_2\text{O}_3$

13. $\text{Y}_2\text{BaCuO}_5 + \text{YCuO}_2 + \text{BaCu}_2\text{O}_2 + \text{Cu}_2\text{O}$

Each of these four-phase combinations are represented in Fig. 4 by the subtetrahedron with the four coexisting phases in the corners. The three-phase combination forms the plane which belongs to the two neighboring subtetrahedrons. According to the phase rule, the oxygen potential within a subtetrahedron is fixed and will change only with temperature.

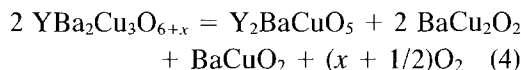
The oxygen potential was measured for the following four-phase combinations:

2. $\text{YBa}_2\text{Cu}_3\text{O}_{6+x} + \text{BaCuO}_2 + \text{BaCu}_2\text{O}_2 + \text{Y}_2\text{BaCuO}_5$

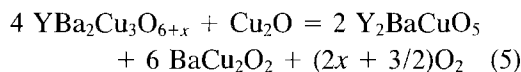
3. $\text{YBa}_2\text{Cu}_3\text{O}_{6+x} + \text{BaCu}_2\text{O}_2 + \text{Cu}_2\text{O} + \text{Y}_2\text{BaCuO}_5$

Reproducible EMF values on these combinations were obtained in less than 1 hr, and remained stable for several hours. Thermodynamic stabilities of the solid phases as related to oxygen partial pressure and temperature are shown in Fig. 5. Above line 2, i.e., at higher oxygen potentials, Y_{123} and Y_{211} are stable in contact with BaCuO_2 . At lower oxygen pressures Y_{123} and Y_{211} are in equilibrium with BaCu_2O_2 or Cu_2O , respectively.

The oxygen potential for combination 2 is given by the reaction



and the thermodynamic stability of BaCu_2O_2 is determined by line 2. For combination 3 the oxygen potential is defined by the reaction



The equilibrium pressures for combinations 4 and 5 are the same and are governed by the $\text{CuO/Cu}_2\text{O}$ equilibrium pressure and

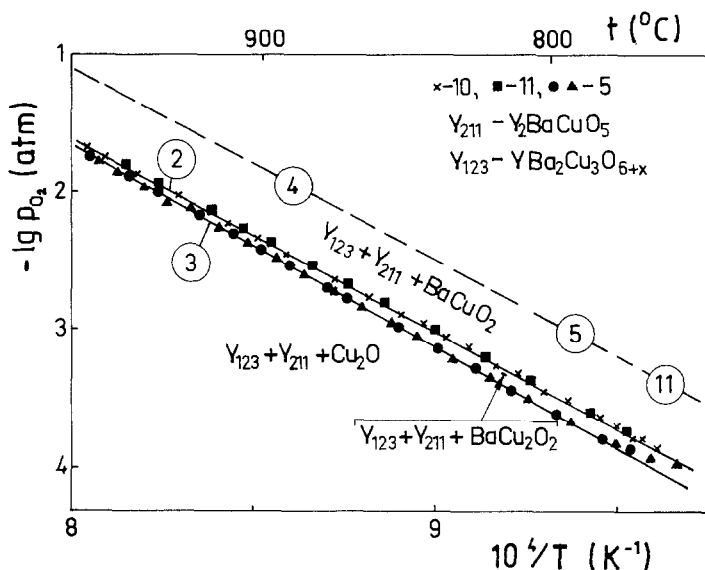


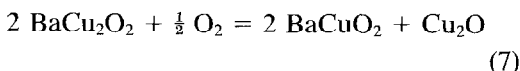
Fig. 5. Oxygen potential for phase combinations (2) and (3) as a function of temperature.

are shown by the dashed line on Fig. 5. Also, the predicted four-phase combination, 11, is controlled by the $\text{CuO}/\text{Cu}_2\text{O}$ equilibrium. The equilibrium pressure for the experimental combination 6 and for the predicted four-phase combination 12 is defined by the reaction



The oxygen potentials for the above reaction have been measured by us in the $\text{Cu}-\text{Cu}_2\text{O}_3-\text{Y}_2\text{O}_3$ system (13).

The oxygen potential for the four-phase combination 1 is defined by the reaction:



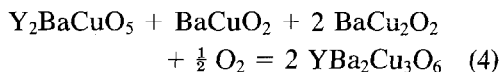
This reaction can be obtained by the arithmetic combination of the Reactions (4) and (5).

The oxygen potential (in atm) for the measured four-phase combinations 2 and 3 may be expressed by the arithmetic expressions obtained by regression analysis of all measurements:

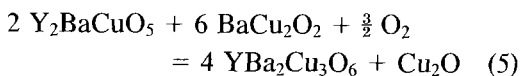
$$2. \log p_{\text{O}_2} = 9.593 - 14013/T$$

$$3. \log p_{\text{O}_2} = 10.204 - 14815/T$$

Assuming the different oxide phases to be stoichiometric the Gibbs energy change for the investigated reactions, (4) and (5), may be calculated:



$$\Delta G_4^0 = -134,154 + 91.84 T \quad (\pm 1100) \text{ (J)}$$



$$\Delta G_5^0 = -425,497 + 293.06 T \quad (\pm 900) \text{ (J)}$$

By a further combination of ΔG_4^0 and ΔG_5^0 the Gibbs energy change for Reaction (7) may be calculated:

$$\Delta G_7^0 = -157,189 + 109.38 T \quad (\pm 1100) \text{ (J)}$$

Acknowledgment

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