

Standard Gibbs free energy of formation of BaCuO_2 and BaCu_2O_2 from oxides

K. Borowiec and K. Kolbrecka

Warsaw University of Technology, Institute of Solid State Technology, ul.
Noakowskiego 3, 00-664 Warsaw (Poland)

(Received January 29, 1991; in final form June 17, 1991)

Abstract

Phase relations in the Cu–CuO–BaO system were studied by the equilibrium and quenching technique. In the temperature range 800–950 °C three cuprates, *i.e.* BaCuO_2 , Ba_2CuO_3 and BaCu_2O_2 , are stable in the system. The thermodynamic stabilities of BaCuO_2 and BaCu_2O_2 were determined by means of the e.m.f. measurements for the following equilibria: $\text{BaCu}_2\text{O}_2(\text{s}) = \text{BaO}(\text{s}) + 2\text{Cu}(\text{s}) + (1/2)\text{O}_2(\text{g})$ and $2\text{BaCuO}_2(\text{s}) + \text{Cu}_2\text{O}(\text{s}) = 2\text{BaCu}_2\text{O}_2(\text{s}) + (1/2)\text{O}_2(\text{g})$. From the data obtained on these three-phase combinations the following relationships were calculated for the Gibbs free energy: $\text{BaO}(\text{s}) + \text{Cu}_2\text{O}(\text{s}) = \text{BaCu}_2\text{O}_2(\text{s})$ with $\Delta G_f^\circ = -30358 + 0.90T$ (J mol⁻¹); and $\text{BaO}(\text{s}) + \text{CuO}(\text{s}) = \text{BaCuO}_2(\text{s})$ with $\Delta G_f^\circ = -42900 + 7.8T$ (J mol⁻¹).

1. Introduction

The determination of phase relations and thermodynamic stability in the Y–Ba–Cu–O system at high temperatures is crucial for the development of an efficient process for fabrication of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$. It is well known that the structure and resistivity of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ that are observed at room temperature depend critically on how the superconducting material is processed at high temperatures. There is also a need from both the academic and the practical point of view to establish the phase stabilities for the three ternary systems which are included in the Y–Ba–Cu–O system.

The most interesting part of the quaternary Y–Ba–Cu–O system may conveniently be illustrated by the tetrahedron shown in Fig. 1. Three oxides, *i.e.* Y_2O_3 , BaO and CuO, and the metallic copper are chosen as the four components and they represent the four corners of the tetrahedron. The present paper describes the phase relations and the results of oxygen potential measurements for a chosen three-phase combination in the Cu–CuO–BaO system. This system forms the side wall of the tetrahedron in Fig. 1.

Within the BaO–CuO system investigated in air three cuprates have been identified. The structure of the first compound, BaCuO_2 , has been determined by Kipka and Muller-Buschbaum [1] by using single-crystal X-ray diffraction. According to a preliminary experimental phase diagram of BaO–CuO in air, investigated by Wong-Ng *et al.* [2], BaCuO_2 melts at 1000 °C, and a second

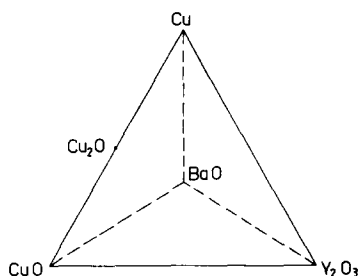


Fig. 1. The Y-Ba-Cu-O system with Y_2O_3 , BaO, CuO and copper as components.

compound, Ba_2CuO_3 , was indicated to exist below 800 °C. Roth *et al.* [3] have observed partial melting of Ba_2CuO_3 at 950 °C. According to de Leeuw *et al.* [4] a single phase of Ba_2CuO_3 can be readily produced by firing a mixture of BaO_2 and CuO in the appropriate ratio at 900 °C, preferably in oxygen. They also found that the samples of Ba_2CuO_3 slowly cooled to room temperature in air had been oxidized to $Ba_2CuO_{3.3}$. The same authors have reported the existence of a third cuprate, *i.e.* $Ba_3Cu_5O_8$, below 800 °C in the CuO-rich part of the system. Recently, this compound has been identified by Thompson *et al.* [5] as $Ba_2Cu_3O_{5+x}$ with a wide range of oxygen non-stoichiometries which causes changes in the related structural forms depending on x . A single phase of $Ba_2Cu_3O_{5+x}$ has been obtained by the authors via the reaction of $2BaO_2 + 3CuO$ in sealed and evacuated silica tubes at 700 °C. Thermoanalysis of $Ba_2Cu_3O_{5+x}$ in oxygen and nitrogen flow and X-ray diffraction patterns of the reduced and oxidized form of $Ba_2Cu_3O_{5+x}$ were presented by Halasz *et al.* [6].

In addition to these cuprates, the next cuprate —*i.e.* Ba_3CuO_4 — has been reported by Frase *et al.* [7] in the BaO–CuO system in air. In our experimental work on the Cu–CuO–BaO system we started by equilibrating samples from the BaO–CuO system in air in the temperature range 800–1000 °C. In this temperature range we did not find evidence for the existence of the last two cuprates, *i.e.* $Ba_2Cu_3O_{5+x}$ and Ba_3CuO_4 .

At lower but undefined oxygen potentials, *i.e.* in argon at 900 °C, a further cuprate, $BaCu_2O_2$, has been obtained from oxides by Teske and Muller-Buschbaum [8]. This phase is strongly hygroscopic and it presents difficulties in the experimental determination of phase relations and in the measurement of oxygen potentials.

2. Experimental details

Copper powder (Merck), Cu_2O (Merck), CuO (the British Drug House) and $BaCO_3$ (Riedel de Haen) were used without further purification to determine the phase relations by the equilibration and quenching technique. First, a mixture of CuO and $BaCO_3$ in the molar ratio 1:2 was fired in air at

950 °C in order to get the single phase of Ba_2CuO_3 . For synthesizing different three-phase combinations three types of starting mixtures, *i.e.* $\text{Ba}_2\text{CuO}_3\text{--Cu}$, $\text{Ba}_2\text{CuO}_3\text{--Cu}_2\text{O}$ and $\text{Ba}_2\text{CuO}_3\text{--Cu--CuO}$, were prepared by mixing Ba_2CuO_3 with calculated amounts of metallic copper powder, Cu_2O or Cu--CuO . The mixing of powders was done in an agate mortar under absolute alcohol. The starting mixtures were annealed in evacuated and sealed silica tubes. In order to exclude any chemical reaction between the silica and the mixtures, 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 for at least 48 h.

All of the investigated compositions, treated in silica tubes, were quenched after heat treatment and examined by the X-ray powder diffraction technique. The standard precaution has been taken in order to avoid the contact of the equilibrated samples which contained hygroscopic BaCu_2O_2 with air during X-ray analysis. The transferring of equilibrated samples from the silica tubes to the calcia-stabilized zirconia ($\text{ZrO}_2(\text{CaO})$) tubes for e.m.f. measurements was eliminated by synthesizing again a given three-phase combination directly in the $\text{ZrO}_2(\text{CaO})$ tubes. It was the most practical way to avoid the decomposition of the hygroscopic specimens by moisture.

This procedure was used for measurements of the oxygen potential for the following three-phase combinations: $\text{Cu--BaCu}_2\text{O}_2\text{--BaO}$ and $\text{Cu}_2\text{O--BaCu}_2\text{O}_2\text{--BaCuO}_2$. In this case, the calculated amounts of Ba_2CuO_3 and copper or Ba_2CuO_3 and Cu_2O were mixed and placed into the $\text{ZrO}_2(\text{CaO})$ tubes together with a platinum lead pressed against the bottom of the tube. Before heating, air inside the $\text{ZrO}_2(\text{CaO})$ tube was swept out by argon and then the cell was heated to 950 °C and was kept at that temperature for 2 days to synthesize the above mentioned three-phase combinations. 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 at atmospheric pressure (see Fig. 2). A platinum lead which served as one leg of a Pt/Rh thermocouple was welded to the gauze.

The e.m.f. values were measured at temperature intervals of 20–30 °C in the range 750–950 °C, and were made repeatedly at decreasing and increasing temperatures. The time needed for the cell e.m.f. to attain a steady value was approximately 6 h. The stability of the e.m.f. was checked by polarizing the cell either by momentarily short circuiting or by exerting a voltage of the opposite sign. After relieving the polarizing sources, the cell e.m.f. quickly recovered its previous steady state value within 1 min. As the rate of the solid state reaction as well as the sensitivity of the $\text{ZrO}_2(\text{CaO})$ electrolyte decreases rapidly below 750 °C this became the lower temperature limit for the e.m.f. measurements. Above 970 °C the e.m.f. values became scattered because of partial melting of the working electrode.

The oxygen partial pressure p_{O_2} inside the reaction mixture is related to the e.m.f. E , temperature T and the oxygen partial pressure of the reference electrode $p_{\text{O}_2}^0$ by the Nernst equation

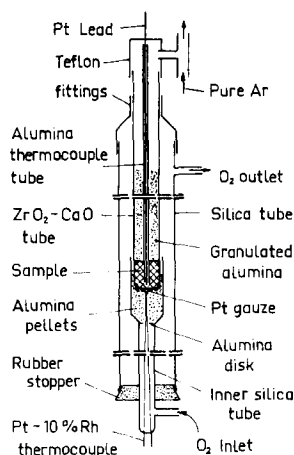


Fig. 2. An e.m.f. cell: the cell is surrounded by a grounded shield and is mounted inside a furnace tube.

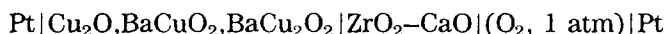
$$\log p_{\text{O}_2} = - \frac{4FE}{2.303RT} + \log p_{\text{O}_2}^0$$

where R is the gas constant, F is the Faraday constant and p_{O_2} is measured in atmospheres. The oxygen partial pressure at the reference electrode could vary slightly around 1 atm due to atmospheric pressure changes.

Successful e.m.f. measurements were made on the following galvanic cell configurations:

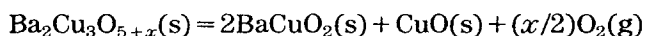


to determine ΔG_f^0 for BaCu_2O_2 , and



to determine Δ_f^0 for BaCuO_2 .

All compositions were calculated in terms of the molar fractions of copper, CuO and BaO and these fractions were used in the subsequent construction of the ternary phase diagram. The compositions of the individual samples on which the e.m.f. measurements were made are shown by dots in Fig. 3, which gives an isothermal section of the phase diagram at 950 °C as deduced from the X-ray analysis as well as the equilibrium oxygen partial pressure for the two three-phase regions as obtained from the e.m.f. work. As was mentioned above, the $\text{Ba}_2\text{Cu}_3\text{O}_{5+x}$ was found to be stable below 800 °C, and above this temperature a peritectic transition occurs according to the reaction



With decreasing temperature the liquid phase in the CuO-rich part of the diagram will disappear at about 900 °C and then, on further cooling below 800 °C, the $\text{Ba}_2\text{Cu}_3\text{O}_{5+x}$ will appear. It means that at the lower temperatures

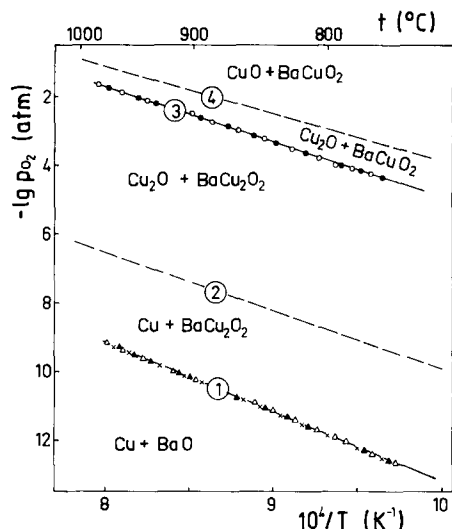
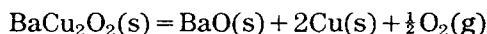
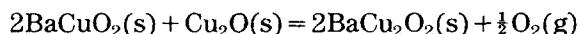


Fig. 4. Oxygen potential for phase combinations (1) and (3) as a function of temperature: \times , composition 1 (in Fig. 3); Δ , composition 2; \blacktriangle , composition 3; \bullet , composition 4; \circ , composition 5.



and line 1 in Fig. 4 is the thermodynamic stability limit of BaCu_2O_2 . The equilibrium pressure for combination (2) is governed by the $\text{Cu}-\text{Cu}_2\text{O}$ equilibrium pressure and it is indicated by the broken line 2. At the full line 3, BaCuO_2 reacts with Cu_2O to form BaCu_2O_2 and determines the oxygen potential for phase combination (3):



The phase combination (4) is less interesting because, below 900 °C where the liquid phase disappears, the oxygen potential over the solid phases is controlled by the $\text{Cu}_2\text{O}-\text{CuO}$ equilibrium.

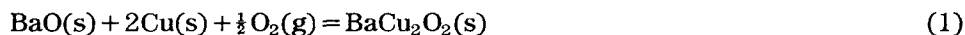
The oxygen partial pressure (atm) for combinations (1) and (3) may be expressed by the arithmetic expressions obtained by regressional analysis of all measurements; for combination (1)

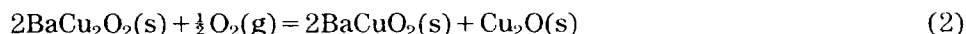
$$\log p_{\text{O}_2} = 7.472 - 20565/T (\pm 0.24)$$

and for combination (3)

$$\log p_{\text{O}_2} = 11.470 - 16552/T (\pm 0.26)$$

Assuming the BaCu_2O_2 and BaCuO_2 to be stoichiometric in the temperature range 750–950 °C, the Gibbs energy change for the investigated reactions may be calculated:





$$\Delta G_2^0 = -158460 + 109.80T \text{ (} \pm 2800 \text{ J mol}^{-1}\text{)}$$

By a further combination of the ΔG_1^0 with the Gibbs energy for the formation of $\text{Cu}_2\text{O}(\text{s})$ [9] the Gibbs energy for the formation of $\text{BaCu}_2\text{O}_2(\text{s})$ was calculated to be



$$\Delta G_3^0 = -30358 + 0.90T \text{ (J mol}^{-1}\text{)}$$

The combination of the ΔG_1^0 with the ΔG_2^0 and the Gibbs energy for the formation of $\text{CuO}(\text{s})$ leads to the Gibbs energy for the formation of $\text{BaCuO}_2(\text{s})$:



$$\Delta G_4^0 = -42900 + 7.80T \text{ (J mol}^{-1}\text{)}$$

Acknowledgment

This work has been supported by the Central Programme for Basic Research (CPBP) 6.6.64 research programme.

References

- 1 R. Kipka and H. Muller-Buschbaum, *Z. Naturforsch., Teil B*, 32 (1977) 121.
- 2 W. K. Wong-Ng, K. L. Davis and R. S. Roth, *J. Am. Ceram. Soc.*, 71 (1988) C-64.
- 3 R. S. Roth, K. L. Davis and J. R. Dennis, *Adv. Ceram. Mater.*, 2 (1987) 303.
- 4 D. M. de Leeuw, C. A. H. A. Mutsaers, C. Langereis, H. C. A. Smoorenburg and P. J. Rommers, *Physica (Utrecht) C*, 152 (1988) 39.
- 5 J. G. Thompson, J. D. FitzGerald, R. L. Withers, P. J. Barlow and J. S. Anderson, *Mater. Res. Bull.*, 24 (1989) 505.
- 6 I. Halasz, V. Fulop, I. Kirschner and T. Porjesz, *J. Cryst. Growth*, 91 (1988) 444.
- 7 K. G. Frase, E. G. Liniger and D. R. Clarke, *J. Am. Ceram. Soc.*, 70 (1987) C-204.
- 8 C. L. Teske and H. Muller-Buschbaum, *Z. Naturforsch., Teil B*, 27 (1972) 296.
- 9 O. Kubaschewski and C. B. Alcock, *Metallurgical Thermochemistry*, 5th edn., Pergamon, Toronto, 1979.