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High-temperature stabilities of $YCuO_2$, $BaCu_2O_2$ and Ba_2CuO_3 from oxide electrolyte e.m.f. measurements

R. PANKAJAVALLI, O. M. SREEDHARAN
Metallurgy Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, Tamil Nadu, India

The oxygen potentials in the system $YCuO_2/Y_2O_3/Cu$ and $Y_2O_3/YCuO_2/CuO$ were measured over the ranges 1113–1255 K and 782–1122 K by employing oxide electrolyte galvanic cells with air/platinum as the reference electrode, and the expression

$$\Delta G^{\circ}_{f,ox}(YCuO_2)(\pm 0.19)(kJ\,mol^{-1}) = -5.346 + 0.00384\,T \quad (K)$$

was determined. Similar e.m.f. measurements were carried out on the electrodes $BaCuO_2/BaCu_2O_2/Cu_2O$ and $Ba_2CuO_3/BaCuO_2/BaCu_2O_2$ were measured over the ranges 1003–1132 K and 1175–1235 K and from the results, the $\Delta G^{\circ}_{f,ox}$ of $BaCu_2O_2$ and Ba_2CuO_3 were determined to be

$$\Delta G^{\circ}_{f,ox}(BaCu_2O_2)(kJ\,mol^{-1}) = -25.09 + 0.01548\,T \quad (K)$$

$$\Delta G^{\circ}_{f,ox}(Ba_2CuO_3)(kJ\,mol^{-1}) = 5.79 - 0.07492\,T \quad (K)$$

1. Introduction

There is considerable interest in the high-temperature thermodynamic characterization of ternary oxides in the Y–Cu–O and Ba–Cu–O systems owing to their relevance to the stabilities of ceramic superconductors such as $YBa_2Cu_3O_{7-x}$ [1, 2]. So far, three ternary oxides, namely $YCuO_2$, $Y_2Cu_2O_5$ and $YCuO_3$, have been reported to be present in the system Y–Cu–O [3–11]. Of these, $YCuO_3$ can exist at higher temperatures only under conditions of oxygen pressures exceeding 100 atm [12–14]. Several investigators have reported oxygen potential measurements on three-phase mixtures bearing the ternary phase $Y_2Cu_2O_5$ by employing the solid electrolyte e.m.f. technique [3–11]. Analysis of these data shows considerable discrepancy in the temperature range of stability of $Y_2Cu_2O_5$ with respect to disproportionation into the constituent oxides Y_2O_3 and CuO. In addition, there is considerable ambiguity in the literature on the stability of $YCuO_2$ phase [6–10] and its temperature range of co-existence with $Y_2Cu_2O_5$ [10]. To resolve this ambiguity, oxygen potential measurements were carried out on two different three-phase mixtures bearing the ternary oxide $YCuO_2$, and the results are presented.

In the Ba–Cu–O system, three ternary oxides, namely $BaCuO_2$, $BaCu_2O_2$ and Ba_2CuO_3 are known to be stable in the range 900–1250 K [1, 11, 15]. Reliable standard Gibbs energy data on $BaCuO_2$ were reported by Zhanguo *et al.* [11] by employing the CaF_2–e.m.f. technique, and by Borowiec and Kolbrecka [15] by the oxide electrolyte e.m.f. method. However, the compounds $BaCu_2O_2$ and Ba_2CuO_3 could not be reliably characterized using similar measurements. Hence, the present investigation was undertaken to facilitate the characterization of $BaCu_2O_2$ and Ba_2CuO_3 using the oxide e.m.f. technique.

2. Experimental procedure

2.1. Materials

High-purity copper (Johnson Mathey), Y_2O_3 (Indian Rare Earths), reagent-grade CuO (E. Merck), reagent-grade anhydrous $BaCO_3$ (E. Merck) and BaO_2 (Aldrich Chemicals, USA) were used as the starting materials. The Cu_2O was prepared by heating CuO in a stream of purified argon at 1273 K for 6 h followed by quenching. An equimolar mixture of Y_2O_3 and Cu_2O was intimately mixed and compacted into cylindrical pellets of 10 mm diameter and 3–4 mm thickness under a pressure of 100 MPa. These pellets were outgassed at 673 K and sealed in silica ampoules after evacuating to a pressure of 1–10 mPa. These were then heated to 1223 K for 20 h followed by furnace cooling. This procedure was repeated twice to ensure completion of the reaction to form $YCuO_2$. Likewise, a mixture of $BaCO_3$ and Cu_2O in the mole ratio of 1 : 1, was compacted into pellets and heated at 1273 K for 24 h in a stream of purified argon to facilitate the formation of $BaCu_2O_2$. However, $BaCuO_2$ and Ba_2CuO_3 could be prepared by heating two different mixtures of BaO_2 and CuO in the mole ratios of 1 : 1 and 2 : 1, respectively, in the form of compacted pellets at 1273 K for 20 h

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in air. For the samples prepared by heating in air or argon, the procedure of heating and compacting into cylindrical pellets was repeated twice. The completion of the reaction in all the three cases was ensured by checking for the absence of impurity phases by X-ray powder diffraction (XRD) within the 5 mass % limit of its detection.

The three-phase electrodes, $Y_2O_3/YCuO_2/Cu$, $BaCuO_2/BaCu_2O_2/Cu_2O$ and $BaCuO_2/BaCu_2O_2/Ba_2CuO_3$, were prepared by compacting nearly equimolar mixtures of the three constituents for each electrode into cylindrical pellets of 10 mm diameter and 2–3 mm thickness at the same 100 MPa pressure. The same procedure was adopted for the preparation of the $Y_2O_3/YCuO_2/CuO$ electrode except that the three phases were taken in a mole ratio of 1:3:1 instead of 1:1:1.

2.2. E.m.f. measurements

The e.m.f. measurements were carried out on the galvanic cells of the following configurations

$$\text{Pt, } Y_2O_3\text{, Cu, } YCuO_2/15\text{ YSZ/air } (P_{O_2} = 0.21\text{ atm}),\text{ Pt} \qquad \text{(I)}$$

$$\text{Pt, } Y_2O_3\text{, } YCuO_2\text{, CuO/15 YSZ/air } (P_{O_2} = 0.21\text{ atm}),\quad \text{Pt} \qquad \text{(II)}$$

$$\text{Pt, } BaCuO_2\text{, } BaCu_2O_2\text{, } Cu_2O/15\text{ YSZ/air } (P_{O_2} = 0.21\text{ atm}),\quad \text{Pt} \qquad \text{(III)}$$

$$\text{Pt, } Ba_2CuO_3\text{, } BaCuO_2\text{, } BaCu_2O_2/15\text{ YSZ/air } (P_{O_2} = 0.21\text{ atm}),\quad \text{Pt} \qquad \text{(IV)}$$

(15 YSZ = 15 wt % yttria-stabilized zirconia)

The one-end-closed solid electrolyte tube was of the dimensions 12 mm outer diameter and 1.5 mm wall thickness and 300 mm long with the closed end flat. A nearly static atmosphere of purified argon was provided for the test-electrode compartment. The temperature was measured using a Pt–10% Rh/Pt thermocouple whose junction was located near the flat end of the electrolyte tube in the air-reference electrode compartment. The reversibility of the e.m.f. readings was ascertained by their reproducibility in thermal cycling. The absence of asymmetric potentials was verified by measuring null e.m.f. using the same cell assembly with air in both the electrode chambers over the experimental temperature range. The equilibrium nature of the e.m.f. was ascertained by a 5–10% variation in the otherwise equimolar ratio of the constituents of the pellets from one experimental run to the other.

3. Results

The results on cells I–IV shown in Figs 1–4 could be represented by the following least squares expressions valid over the temperature ranges given in parentheses

$$E_{\text{I}}(\pm 2.1)(\text{mV}) = 887.66 - 0.42274\,T(\text{K}) \qquad (1)$$
$$(1113\text{–}1255\text{ K})$$

$$E_{\text{II}}(\pm 1.8)(\text{mV}) = 647.29 - 0.50249\,T\text{ (K)} \qquad (2)$$
$$(782\text{–}1122\text{ K})$$

$$E_{\text{III}}(\pm 1.7)(\text{mV}) = 442.74 - 0.24715\,T\text{ (K)} \qquad (3)$$
$$(1003\text{–}1132\text{ K})$$

$$E_{\text{IV}}(\pm 2.2)(\text{mV}) = 1267.79 - 0.96947\,T\text{ (K)} \qquad (4)$$
$$(1175\text{–}1235\text{ K})$$

4. Discussion

4.1. The high-temperature stability of $YCuO_2$

For the computation of the standard Gibbs energy of formation, $\Delta G^{\circ}_{\text{f,ox}}$ of $YCuO_2$, the e.m.f. results on cell I given by Equation 1 could be combined with the e.m.f. results on the cell

$$\text{Pt, Cu, } Cu_2O\,|\,15\text{ YSZ}\,|\,\text{air } (P_{O_2} = 0.21\text{ atm}),\text{ Pt} \qquad \text{(V)}$$

$$E_{\text{V}}\ (\pm 1.1)(\text{mV}) = 863.68 - 0.40917\,T \quad \text{(K)} \qquad (5)$$

reported earlier by Mallika [16] using the same experimental equipment. This procedure would minimize systematic errors in such galvanic cell measurements. The result of such a combination of Equations 1 and 5 would yield the expression

$$E_{\text{VI}} = E_{\text{I-V}}(\pm 3.2)(\text{mV}) = 23.98 - 0.01357\,T \quad \text{(K)} \quad (3)$$

for the hypothetical cell

$$\text{Pt, } Y_2O_3\text{, Cu, } YCuO_2\,\|\,\text{Cu, } Cu_2O\text{, Pt} \qquad \text{(VI)}$$

For the passage of 1 faraday of electricity, the over-all reaction for cell VI would be

$$1/2\,Y_2O_3(s) + 1/2\,Cu_2O(s) \rightleftharpoons YCuO_2(s) \qquad (7)$$

The corresponding standard Gibbs energy change, $\Delta G^{\circ}_{\text{R}}$, obtained from Nernst equation would be identical to $\Delta G^{\circ}_{\text{f,ox}}$ ($YCuO_2$) and is given by

$$\Delta G^{\circ}_{\text{f,ox}}(YCuO_2)(\pm 0.31)(\text{kJ mol}^{-1}) = -2.318 + 0.00131\,T \quad \text{(K)} \qquad (8)$$

After correcting for the standard state of oxygen in the reference air/platinum electrode of cell II, the over-all cell reaction for the passage of 4 faraday of electricity could be represented as follows

$$4\,YCuO_2(s) + O_2(g) \rightleftharpoons 2\,Y_2O_3(s) + 4CuO(s) \qquad (9)$$

The corresponding expression for $\Delta G^{\circ}_{\text{R(9)}}$ for the cell II was found to be

$$(\Delta G^{\circ}_{\text{R(9)}} \pm 0.69)(\text{kJ mol}^{-1}) = -249.82 + 0.19394\,T \quad \text{(K)} \qquad (10)$$

Combining Equation 10 with the literature data for the oxygen potential ($RT\ln P_{O_2}$) for the system Cu_2O/CuO compiled by Kubaschewski and Alcock [17], the following expression for the $\Delta G^{\circ}_{\text{f,ox}}$ ($YCuO_2$) could be derived

$$\Delta G^{\circ}_{\text{f,ox}}(YCuO_2)\,(\pm 2.69)(\text{kJ mol}^{-1}) = -5.168 + 0.00364\,T \quad \text{(K)} \qquad (11)$$

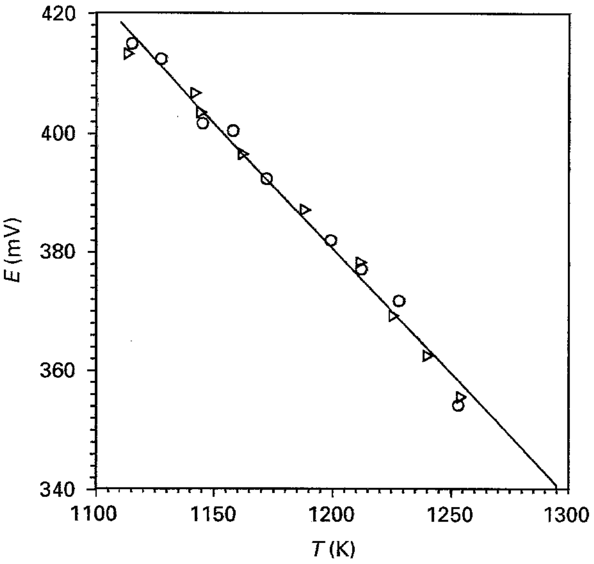

Figure 1 Temperature dependence of the e.m.f. of cell I. (○, ▷) Different experimental runs.

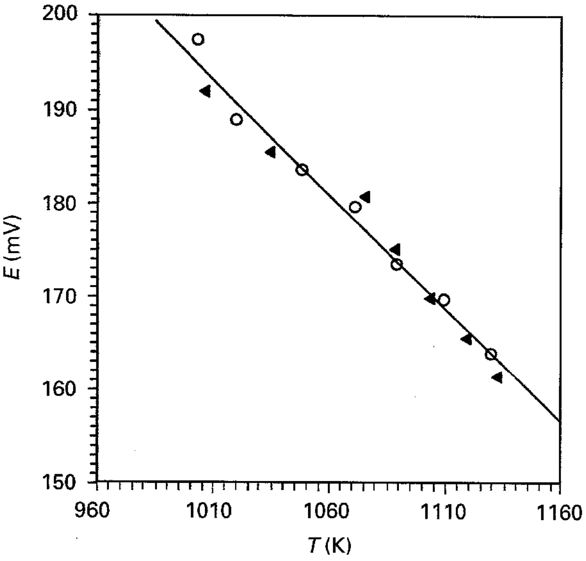

Figure 3 Temperature dependence of the e.m.f. of cell III. (○, ◀) Different experimental runs.

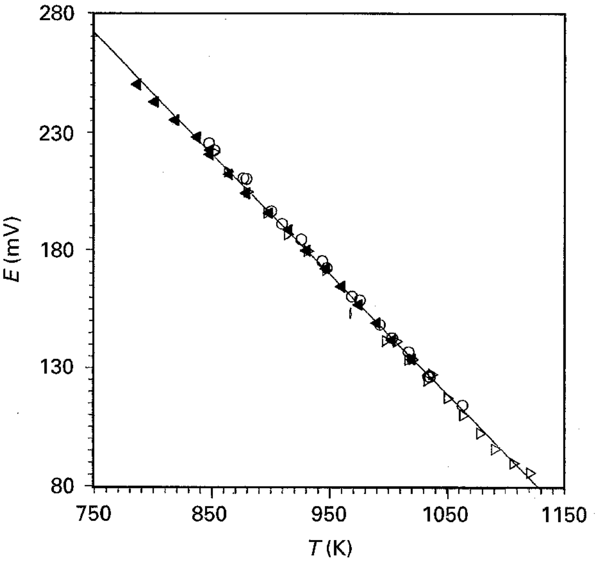

Figure 2 Temperature dependence of the e.m.f. of cell II. (○, ▷, ◀) Different experimental runs.

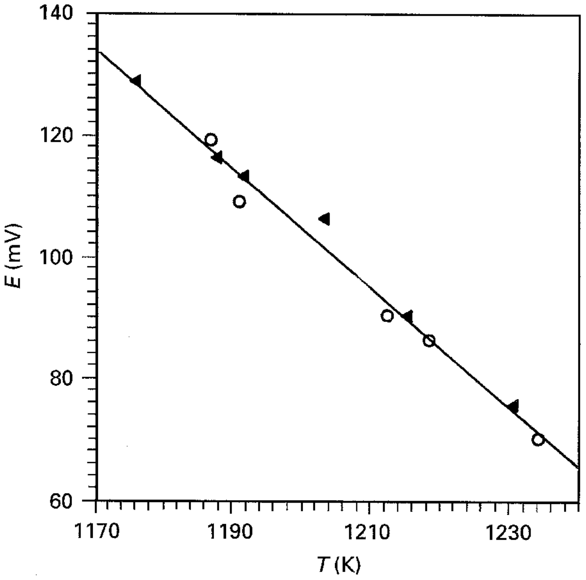

Figure 4 Temperature dependence of the e.m.f. of cell IV. (◀, ○) Different experimental runs.

The least-squares expression (Equation 8) was derived from 18 values of e.m.f. of cell I covering the range 1113–1255 K, whereas Equation 11 was obtained from 53 points for cell II measured over 782–1122 K. The interpolated values at 1100 K for $\Delta G^\circ_{f,ox}$ of $YCuO_2$ derived from Equations 8 and 11 are -0.88 and $-1.17\ kJ\ mol^{-1}$, respectively, showing very good agreement between them. The agreement is even better at 1200 K, as seen from the values of -0.75 and $-0.80\ kJ\ mol^{-1}$ from Equations 8 and 11, respectively. However, the agreement is apparently not so good in a term-wise comparison of enthalpies and entropies from these equations. In fact, the uncertainties in the e.m.f. values of cells I and II could be taken into account in the derivation of $\Delta G^\circ_{f,ox}$ ($YCuO_2$) only if a combined least squares expression could be derived for all the 71 experimental points taken together. This was accomplished by computing values of ΔG°_f of Cu_2O for each of the 18 values of temperature for which e.m.f. values were available and then calculating corresponding values of $\Delta G^\circ_{f,ox}$ of $YCuO_2$. The same procedure was repeated in the case of cell II by interpolating values of $RT\ln P_{O_2}$ for CuO/Cu_2O from the literature [17]. The combined least squares expression for the 71 points could thus be computed to be as follows

$$\Delta G^\circ_{f,ox}(YCuO_2)(\pm 0.19)(kJ\ mol^{-1}) = -5.346 + 0.003\,84\ T(K) \qquad (12)$$

valid over the extended range of 782–1255 K. A comparison of Equation 12 with similar expressions reported in the literature is shown in Table I. At the mean temperature (1020 K) of our measurements, the values of $\Delta G^\circ_{f,ox}$ of $YCuO_2$ seem to be unreasonably high from the investigations by Borowiec and Kolbrecka (-28 kJ) [7] and Wiesner *et al.* (-58 kJ) [9]. As per the expressions of Kale and Jacob [6] and this

TABLE I $\Delta G^{o}_{f,ox}$ ($YCuO_2$) from e.m.f. measurements

	$\Delta G^{o}_{f,ox}$ = (kJ mol^{-1}) $A + BT$ (K)		T range	$T^{a}_{decomp.}$	$\Delta G^{o}_{f,ox}$(kJ mol^{-1})	Reference
	A	B	(K)	(K)	at 1020 K	
1.	− 5.79	0.0039	873–1323	1488 (U)	− 1.8	[6]
2.	− 5.35	0.0038	782–1255	1393 (U)	− 1.4	Present work
3.	− 32.98	0.0049	1023–1273	–	−27.9	[7]
4.	− 61.13	0.0027	973–1223	–	−58.4	[9] [b]
5.	13.29	− 0.0120	1023–1173	1106 (L)	+ 1.0	[10] [c]
6.	12.05	− 0.0108	1115–1273	1116 (L)	+ 1.0	[8]

[a] U, Upper limit of temperature for dissociation; L, lower limit of temperature for dissociation.

[b] TG/OCT (oxygen coulometric titration) techniques.

[c] From OCT technique.

TABLE II $\Delta G^{o}_{f,ox}$($Y_2Cu_2O_5$) from e.m.f. measurements

	$\Delta G^{o}_{f,ox}$ (kJ mol^{-1}) = $A + B\,T$ (K)		T range	T_d	$\Delta G^{o}_{f,ox}$ (kJ mol^{-1}) at 1000 K	Reference
	A	B	(K)	(K)		
1.	21.24	− 0.022 81	1173–1340	931	− 6.1	[3][a]
2.	10.91	− 0.013 41	1097–1292	814	− 5.2	[4][a]
3.	12.75	− 0.017 14	1025–1220	744	− 7.8	[5][a]
4.	34.25	− 0.036 48	953–1110	939	− 9.5	[8][a]
5.	11.21	− 0.015 07	873–1323	744	− 6.9	[6][b]
6.	− 72.58	+ 0.004 24	1023–1273	–	− 67.5	[7][b, c]
7.	18.47	− 0.021 9	861–980	843	− 7.8	[19][d]
8.	14.30	− 0.017	950–1200	865	− 6.1	[11][d]
9.	− 19.45	+ 0.003 56	973–1223	–	− 15.2	[9][e]
10.	80.36	− 0.077 4	1023–1173	1038	− 12.5	[10][e]

[a] $Y_2O_3/Cu_2O/Y_2Cu_2O_5$ electrode.

[b] $Y_2O_3/YCuO_2/Y_2Cu_2O_5$ electrode.

[c] Either as footnote (b) or with Cu_2O in place of Y_2O_3.

[d] CaF_2–e.m.f. technique in 1 atm O_2.

[e] From TG/OCT (oxygen coulometric titration) measurements.

work, $YCuO_2$ has an upper temperature limit of stability towards dissociation into Y_2O_3 and Cu_2O and not a lower temperature limit, as predicted by Konetzki and Schmid-Fetzer [10] and Suzuki *et al.* [8]. Konetzki and Schmid-Fetzer employed coulometry which could give rise to polarization or composition inhomogeneity at the interface, especially when ternary compounds were studied. These authors observed non-equilibrium mixtures of four phases by quenching after resorting to oxygen coulometric titration (OCT). They attributed the presence of four phases (instead of three) to non-attainment of equilibrium owing to marginal stability of $YCuO_2$ over Y_2O_3 and Cu_2O. However, these non-equilibrium conditions could well be due to a coulometrically produced fourth phase not becoming reversed owing to smaller values of the Gibbs energy changes (driving force for the reverse reaction). Further, the lower temperature limit of stability predicted, by the last two groups of authors, as 1106–1116 K, should be taken to be equivalent to stating that $YCuO_2$ is entropy stabilized at higher temperatures. This is contradictory to the observation of the existence of upper temperature limits of stability (but not lower limits) of isomorphous $LnCuO_2$ compounds (Ln = La to Gd) during their synthesis by Haas and Kordes [18]. The other two sets of data in the table are indicative of $YCuO_2$ being stable over the entire temperature range of existence of solids. Kale and Jacob [6] had predicted the co-existence of $YCuO_2$ with Y_2O_3 and CuO from room temperature up to 744 K beyond which $Y_2Cu_2O_5$ would co-exist with $YCuO_2$. If $YCuO_2$ is assumed to be stable from room temperature up to 1400 K, as predicted by Kale and Jacob [6], and this work, then the set of phases co-existing with $Y_2Cu_2O_5$ should be $YCuO_2/Y_2O_3$ or $YCuO_2/Cu_2O$ but not Y_2O_3/Cu_2O. Therefore, the phase mixture $Y_2Cu_2O_5/Y_2O_3/Cu_2O$ employed by Tretyakov *et al.* [3] (1173–1390 K), Pankajavalli and Sreedharan [4] (1097–1292 K) and Shimpo and Nakamura [5] (1025–1220 K) should only be showing metastable co-existence in order to fix the oxygen potential. When this metastable co-existence is possible at higher temperatures, the equilibrium between the phases $YCuO_2/Y_2O_3/CuO$ should also be extendable to above 744 K [5, 6], 814 K [4] or even 931 K [3] (the threshold temperature for the formation of $Y_2Cu_2O_5$ as determined earlier). This proposition could be confirmed by measuring reproducible e.m.f. values for cell II despite the metastable co-existence of Y_2O_3 and CuO with $YCuO_2$. As in the case of $YCuO_2$, there is considerable scatter in the values of T_d reaction temperature for the formation of $Y_2Cu_2O_5$ from Y_2O_3 and CuO (cf. Table II). Unlike $YCuO_2$, there is relatively less ambiguity regarding at least the exothermicity or endothermicity of the reaction if one chooses to omit the rather high values of − 20 and − 73 kJ mol^{-1} for $\Delta H^{o}_{f,ox}$ of $Y_2Cu_2O_5$ reported by Wiesner *et al.* [9] and Borowiec and Kolbreca [7].

The $\Delta H^\circ_{f,ox}$ ($Y_2Cu_2O_5$) is seen to be in the range 11–21 kJ mol^{-1} and $\Delta S^\circ_{f,ox}$ is about 13–23 J K^{-1} mol^{-1}. There is one reliable determination of $\Delta H^\circ_{f,ox}$ ($Y_2Cu_2O_5$) reported by Zhou and Navrotsky [20] using high-temperature solution calorimetry according to which the formation of $Y_2Cu_2O_5$ (s) is definitely endothermic with a value of 12.1 ± 2.7 kJ mol^{-1}. This is in good agreement with six out of the ten values listed in Table II. Within those limits for $\Delta H^\circ_{f,ox}$ and $\Delta S^\circ_{f,ox}$ ($Y_2Cu_2O_5$), the theoretical value for T_d below which $Y_2Cu_2O_5$ cannot be formed from Y_2O_3 and CuO, may be taken to lie in the range 744–931 K. Brosha *et al.* [21] reported a value of 955 K as a minimum temperature to which a freeze-dried mixture of Y_2O_3 and CuO (obtained from nitrate precursors) should be heated for the formation of $Y_2Cu_2O_5$. This value (955 K) could also be considered as reasonable in view of the sluggishness of the reaction exploited in the form of their co-existence with $YCuO_2$ in cell II.

The consistency in the data on $\Delta G^\circ_{f,ox}$ ($YCuO_2$) with the oxygen potential measurements on ($Y_2Cu_2O_5$)/Y_2O_3/Cu_2O (under metastable equilibrium) reported by Pankajavalli and Sreedharan [4] and on the electrode bearing the equilibrium mixture $Y_2Cu_2O_5$/$YCuO_2$/Y_2O_3 reported by Kale and Jacob [6] was verified in terms of e.m.f. values of appropriate galvanic cells interpolated at 1000 and 1100 K. The excellent agreement between the measured and computed values of e.m.f. given under entry number 5 in Table III show the $\Delta G^\circ_{f,ox}$ data on $Y_2Cu_2O_5$ from this work are consistent with those on $Y_2Cu_2O_5$ reported earlier by the same authors.

4.2. Thermodynamic stability of $BaCu_2O_2$ and Ba_2CuO_3

After correcting for the standard state of oxygen in the air/platinum reference electrode of cell III, the over-all reaction for the passage of 2 faraday of electricity could be represented as

$$BaCu_2O_2(s) + 1/2O_2(g) \rightleftharpoons BaCuO_2(s) + 1/2Cu_2O(s) \qquad (13)$$

The corresponding expression for $\Delta G^\circ_{R(13)}$ was derived to be

$$\Delta G^\circ_{R(13)}(\pm 0.32)(\mathrm{kJ\,mol^{-1}}) = -85.44 + 0.04119\,T \quad (\mathrm{K}) \qquad (14)$$

valid over the range 1003–1132 K. The magnitude of the $\Delta \bar{S}^\circ_{O_2}$ term in Equation 14, namely 82 J K^{-1} mol^{-1} is considerably smaller than theoretical expectations for reasons which are not presently known. However, Borowiec and Kolbreca [15] reported the following

$$\Delta G^\circ_{R(13)}(\pm 2.8)(\mathrm{kJ\,mol^{-1}}) = -158.46 + 0.10980\,T \quad (\mathrm{K}) \qquad (15)$$

$$(1023\text{–}1223\ \mathrm{K})$$

At 1068 K, which is the mean temperature of validity of Equation 14, the values of ΔG°_R for Reaction 13 calculated from Equations 14 and 15 are -41.4 and -41.2 kJ mol^{-1}, respectively. Thus, the agreement in the ΔG°_R values between the two sets of measurements should be considered as very good within the narrow temperature ranges (about 200 K) covered by the experimental runs. However, the entropy term in Equation 15 is on the higher side of normally expected values of $\Delta \bar{S}_{O_2}$. To derive $\Delta G^\circ_{f,ox}$ of one of the ternaries ($BaCuO_2$ or $BaCu_2O_2$), the values for that of the other must be known. Because a couple of reports [11, 15] employing solid-state galvanic cells are available on $BaCuO_2$, the Gibbs energy data on this compound could be used to evaluate $\Delta G^\circ_{f,ox}$ ($BaCu_2O_2$). Borowiec and Kolbreca [15] as well as Zhanguo *et al.* [11] had reported numerical expressions for $\Delta G^\circ_{f,ox}$ ($BaCuO_2$) and these are compared in Table IV. Despite very good agreement between the two sets of data, the data obtained by oxide e.m.f. were chosen for further calculations in order to minimize systematic errors. It should be mentioned that the results by Azad *et al.* [19] on $\Delta G^\circ_{f,ox}$ ($BaCuO_2$), determined by a CaF_2–e.m.f. technique, were rejected owing to their use of another ternary oxide system as a reference electrode which could retard attainment of equilibrium. Thus, by combining the equation under

TABLE IV $\Delta G^\circ_{f,ox}$ ($BaCuO_2$) from e.m.f.

	$\Delta G_{f,ox}$(kJ mol^{-1}) $= A + BT$(K)		T Range (K)	$\Delta G_{f,ox}$ at 1100 K	Reference
	A	B			
1.	−43.9	+0.0073	950–1200	−35.9	[11][a]
2.	−42.9	+0.0078	1023–1223	−34.3	[15][b]

[a] CaF_2-based galvanic cells.
[b] Stabilized zirconium-based galvanic cells.

TABLE III Internal consistency check for galvanic cells using $YCuO_2$ or $Y_2Cu_2O_5$ in the test electrode

	Galvanic cell	e.m.f. (mV) at		Reference and remarks
		1000 K	1100 K	
1.	Pt, $Y_2Cu_2O_5$, Y_2O_3, Cu_2O ‖ air, Pt	173.6	126.6	Directly measured [4]
2.	Pt, $YCuO_2$, Y_2O_3, Cu ‖ Cu_2O, Cu, Pt	15.6	11.7	Calculated from Equation 12 using Nernst equation (present work)
3.	Pt, $Y_2Cu_2O_5$, $YCuO_2$, Y_2O_3 ‖ Cu_2O, CuO, Pt	0.3	12.2	Directly measured [6]
4.	Pt, Cu_2O, CuO ‖ air, Pt	160.7	106.7	[17]
5.	Pt, $Y_2Cu_2O_5$, Y_2O_3, $YCuO_2$ ‖ air, Pt	158.0	114.9	Combining entries 1 and 2
		161.0	118.9	Combining entries 3 and 4

entry number 2 in Table IV with ΔG_R^o of Equation 14 and $RT\ln P_{O_2}(Cu_2O/CuO)$ from the literature [17], the expression for $\Delta G_{f,ox}^o$ ($BaCu_2O_2$) was calculated and is given as follows

$$\Delta G_{f,ox}^o(BaCu_2O_2)(kJ\,mol^{-1})$$
$$= -25.09 + 0.01548\,T \quad (K) \qquad (16)$$

Borowiec and Kolbreca [15] also reported the following expression for the same by e.m.f. measurements on the electrode $BaCu_2O_2/BaO/Cu$ with air/platinum as the reference electrode over the range 1023–1223 K.

$$\Delta G_{f,ox}^o(BaCu_2O_2)(kJ\,mol^{-1})$$
$$= -30.36 + 0.0009\,T \quad (K) \qquad (17)$$

At 1068 K, values of -8.6 and $-29.4\,kJ\,mol^{-1}$ could be calculated from Equations 16 and 17 which are obviously in disagreement, and require an explanation. From the literature [22], it is seen that the ternary oxide $BaZrO_3$ is extremely stable and is readily formed by the reaction between BaO and ZrO_2. Thus the free BaO in the ternary electrode, $BaCu_2O_2/BaO/Cu$ used by these authors [15] could give rise to mixed potentials by its reaction with ZrO_2 present in the electrolyte, thereby leading to disagreement. In the light of this, the data represented by Equation (16) should be considered as more reasonable and hence used in the subsequent analysis.

The least-squares Equation 4 for the e.m.f. results on cell IV was converted in the same manner as given earlier into ΔG_R^o for the standard cell reaction

$$Ba_2CuO_3(s) + BaCu_2O_2(s) + 1/2\,O_2(g)$$
$$\rightleftharpoons 3BaCuO_2(s) \qquad (18)$$

and is given as follows

$$\Delta G_{R(17)}^o(\pm 0.43)(kJ\,mol^{-1})$$
$$= -244.65 + 0.18058\,T \quad (K) \qquad (19)$$

Combining Equations 19, 16 and that under entry number 2 of Table IV with $RT\ln P_{O_2}$ (Cu_2O/CuO) [17], the following expression was derived to represent $\Delta G_{f,ox}^o$ (Ba_2CuO_3)

$$\Delta G_{f,ox}^o(Ba_2CuO_3)(kJ\,mol^{-1})$$
$$= 5.79 - 0.07492\,T \quad (K) \qquad (20)$$

The expression is valid for a rather narrow temperature range of 1175–1235 K. At the mean temperature of 1205 K, a value of $-84.5\,kJ\,mol^{-1}$ could be derived for $\Delta G_{f,ox}^o$ (Ba_2CuO_3). Because there are no other measurements of Gibbs energy data given in the literature on Ba_2CuO_3, no comparison could be made. However, the large positive value of entropy, namely $75\,JK^{-1}\,mol^{-1}$, is indicative of the existence of Ba_2CuO_3 as a liquid. Although Roth *et al.* [23] reported partial melting at 1223 K, eutectic lowering of the melting point of Ba_2CuO_3 could have taken place to facilitate its existence as a liquid over the temperature interval 1175–1235 K in the electrode mixture $Ba_2CuO_3/BaCuO_2/BaCu_2O_2$. The used pellet gave the appearance of partial melting.

5. Conclusion

The ternary oxides in the Y–Cu–O system, namely $YCuO_2$ are only marginally stable with respect to their dissociation into constituent binary oxides in the temperature range amenable to solid electrolyte measurements. Owing to their somewhat small magnitudes of $\Delta G_{f,ox}^o$, they give rise to metastable co-existence of phases. Nevertheless, even such metastable co-existent mixtures could be used to measure $\Delta G_{f,ox}^o$ of these oxides, and to compare them with stable equilibrium mixtures in order to explain the scatter in the literature data. The reliability of the data so derived for $\Delta G_{f,ox}^o$ ($YCuO_2$) was evaluated by its consistency with that on $Y_2Cu_2O_5$. In the Ba–Cu–O system, $\Delta G_{f,ox}^o$ of Ba_2CuO_3 and $BaCu_2O_2$ was measured by adopting suitable galvanic cell configurations, as reported in this work.

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References

1. D. J. WHITLER and S. R. ROTH (eds), "Phase diagrams for High T_C superconductors". (The American Ceramic Society, Westerville OH, 1991) pp. 41–89.
2. A. M. AZAD and O. M. SREEDHARAN, *Supercond. Sci. Technol.* 3 (1990) 159.
3. YU. D. TRETYAKOV, A. R. KAUL and N. V. MAKUKHIN, *J. Solid State Chem.* **17** (1976) 183.
4. R. PANKAJAVALLI and O. M. SREEDHARAN, *J. Mater. Sci. Lett.* 7 (1988) 714.
5. R. SHIMPO and Y. NAKAMURA, *J. Jpn Inst. Metals Sendai* **54** (1990) 549.
6. G. M. KALE and K. T. JACOB, *Chem. Mater.* **1** (1989) 515.
7. K. BOROWIEC and K. KOLBRECKA, *J. Less-Common Metals.* **163** (1990) 143.
8. R. O. SUZUKI, S. OKADA, T. OISHI and K. ONO, *Mater. Trans. JIM* **31** (1990) 1078.
9. U. WIESNER, G. KRABBES and M. RITSCHEL, *Mater. Res. Bull.* **24** (1989) 1261.
10. R. A. KONETZKI and R. SCHMID-FETZER, *J. Solid State Chem.* **114** (1995) 420.
11. F. ZHANGUO, J. CHUNLIN and Z. ZHONGXIAN, *J. Less-Common Metals* **161** (1990) 49.
12. M. ARJOMAND and D. J. MACHIN, *J. Chem. Soc. Dalton Trans.* (1975) 1061.
13. O. M. SREEDHARAN, C. MALLIKA and K. SWAMINATHAN, *J. Mater. Sci.* **23** (1988) 2735.
14. J. F. BRINGLEY and I. B. M. THOMAS, J. Watson Research Center, New York, private communication (1989).
15. K. BOROWIEC and K. KOLBRECKA, *J. Alloys Compounds* **176** (1991) 225.

16. C. MALLIKA, Ph D thesis, University of Madras, India (1989).
17. O. KUBASCHEWSKI and C. B. ALCOCK, "Metallurgical Thermochemistry", 5th Edn (Pergamon Press, Oxford, 1983).
18. H. HASS and E. KORDES, *Zr. Kristallogr.* **129** (1969) 259.
19. A. M. AZAD, O. M. SREEDHARAN and K. T. JACOB, *J. Mater. Sci.* **26** (1991) 3374.
20. Z. ZHOU and A. NAVROTSKY, *J. Mater. Res.* **7** (1992) 2920.
21. E. L. BROSHA, F. H. GARZON, I. D. RAISTRIC and P. K. DAVIES, *J. Am. Ceram. Soc.* **77** (1994) 1139.
22. V. A. LEVITSKII, *J. Solid State Chem.* **25** (1978) 9.
23. R. S. ROTH, K. L. DAVIS and J. R. DENNIS, *Adv. Ceram. Mater.* **2** (3B) (1987) 303.

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