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# Standard Gibbs' energies of formation of $BaCuO_2$, $Y_2Cu_2O_5$ and $Y_2BaCuO_5$

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The Gibbs' energies of formation of $BaCuO_2$, $Y_2Cu_2O_5$ and $Y_2BaCuO_5$ from component oxides have been measured using solid state galvanic cells incorporating $CaF_2$ as the solid electrolyte under pure oxygen at a pressure of $1.01 \times 10^5$ Pa

$$\langle BaO\rangle + \langle CuO\rangle \rightarrow \langle BaCuO_2\rangle$$

$$\Delta G^\circ_{f,ox}(\pm 0.3)\ (kJ\ mol^{-1}) = -63.4 - 0.0525\ T\ (K)$$

$$\langle Y_2O_3\rangle + 2\langle CuO\rangle \rightarrow \langle Y_2Cu_2O_5\rangle$$

$$\Delta G^\circ_{f,ox}(\pm 0.3)\ (kJ\ mol^{-1}) = 18.47 - 0.0219\ T\ (K)$$

$$\langle Y_2O_3\rangle + \langle BaO\rangle + \langle CuO\rangle \rightarrow \langle Y_2BaCuO_5\rangle$$

$$\Delta G^\circ_{f,ox}(\pm 0.7)\ (kJ\ mol^{-1}) = -72.5 - 0.0793\ T\ (K)$$

Because the superconducting compound $YBa_2Cu_3O_{7-\delta}$ coexists with any two of the phases CuO, $BaCuO_2$ and $Y_2BaCuO_5$, the data on $BaCuO_2$ and $Y_2BaCuO_5$ obtained in this study provide the basis for the evaluation of the Gibbs' energy of formation of the 1–2–3 compound at high temperatures.

## 1. Introduction

Since the discovery of superconductivity in the quarternary ceramic oxide $YBa_2Cu_3O_{7-\delta}$(1–2–3) compound by Wu *et al.* [1] in 1987, systematic studies on thermodynamic characterization of phases in the $YO_{1.5}$–BaO–CuO system have been reported [2–9]. An isothermal section of the phase diagram of this system in air at 1223 K has been reported by several investigators [10–15]. A representative phase diagram reported recently by Jacob and Waseda [15] is shown in Fig. 1. Although there is a considerable disagreement regarding stable phases in the pseudobinary $YO_{1.5}$–BaO among the various investigators, there is a general consensus regarding the phases that coexist with the 1–2–3 compound. The 1–2–3 compound has been found to coexist with any two of the phases CuO, $BaCuO_2$ and $Y_2BaCuO_5$. Hence for the thermodynamic characterization of 1–2–3 compound, it is necessary to determine the thermodynamic stability of $BaCuO_2$ and $Y_2BaCuO_5$. The quarternary oxide $Y_2BaCuO_5$ has been found to coexist with $Y_2Cu_2O_5$ and CuO (or $Y_2O_3$). Therefore, the Gibbs' energy of formation of $Y_2Cu_2O_5$ is also required for thermodynamic characterization of the 1–2–3 compound.

Pankajavalli and Sreedharan [4] have determined the standard Gibbs' energy of formation of $Y_2Cu_2O_5$, in metastable equilibrium with $Cu_2O$ and $Y_2O_3$, using an oxide solid electrolyte over the temperature range 1097–1292 K. Their results are in fair agreement with the values reported by Tretyakov *et al.* [16] and more recently by Kale and Jacob [3], both employing a solid state e.m.f. technique. The stability of $Y_2BaCuO_5$ over the range 717–1021 K has been determined by Pankajavalli and Sreedharan [6] from oxygen potential measurements over the phase mixture $Y_2BaCuO_5 + Y_2BaO_4 + Cu_2O$. Measurements of Gibbs' energy of formation of $BaCuO_2$ have not thus far been reported in the literature; this paper reports these measurements for $BaCuO_2$, $Y_2Cu_2O_5$ and $Y_2BaCuO_5$ using solid state cells incorporating $CaF_2$ as the solid electrolyte. The condensed phase electrodes were equilibrated with pure oxygen at a pressure of $1.01 \times 10^5$ Pa.

## 2. Experimental procedure

### 2.1. Materials

Reagent grade anhydrous $BaCO_3$ (purity > 99.5%), $Y_2O_3$ (purity > 99.99%), CuO (purity > 99.8%) and $ZrO_2$ (purity > 99.99%) were used as the starting materials. Fluorides of barium and yttrium of purity higher than 99.99% were used. Single crystals of $CaF_2$, 10 mm diameter and 3–4 mm, thick, were procured.



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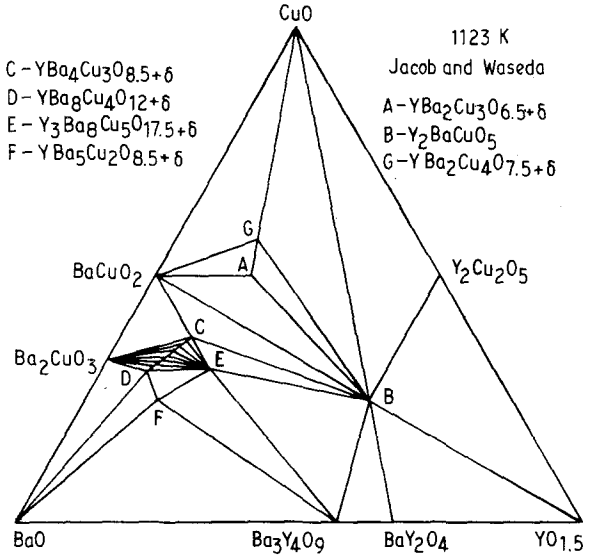


*Figure 1* Isothermal section of the $YO_{1.5}$–BaO–CuO phase diagram at 1123 K.

An intimate mixture of $BaCO_3$ and $ZrO_2$ in the molar ratio of 2:3 was compacted into cylindrical discs of 10 mm diameter and 3–4 mm thickness under a pressure of 100 MPa. These pellets were calcined in air at 1273 K for 24 h. The pellets were ground into a fine powder and the procedure was repeated two or three times to ensure the completion of the solid-state reaction. The product was identified as a two-phase mixture of $BaZrO_3$ and $ZrO_2$ by powder X-ray diffraction (XRD). No free BaO or $BaCO_3$ were detected in the final product.

Equimolar two-phase mixtures containing $BaCuO_2$ + CuO, $Y_2Cu_2O_5$ + CuO and $Y_2BaCuO_5$ + CuO were prepared by taking appropriate starting materials in the required proportions. A summary of experimental conditions used for the synthesis of oxide mixtures is given in Table I. The electrodes were prepared by mixing the oxide mixtures with the corresponding stable fluorides. The compositions of the electrodes are given in Table II. All the mixtures were individually compacted at a pressure of 100 MPa into cylindrical pellets of 10 mm diameter and 2–3 mm thickness to serve as electrodes.

TABLE II Composition of electrodes

| Material(s) | Coexisting fluoride | Weight ratio |
|---|---|---|
| $BaZrO_3 + ZrO_2$ | $BaF_2$ | 1:1:1 |
| $BaCuO_2 + CuO$ | $BaF_2$ | 1:1:1 |
| $Y_2Cu_2O_5 + CuO$ | $YF_3$ | 1:1:1 |
| $Y_2BaCuO_5 + CuO + Y_2Cu_2O_5$ | $BaF_2$ | 1:1:1:1 |
| $Y_2O_3$ | $YF_3$ | 3:1 |

## 2.2. E.m.f. measurements

A stacked-pellet assembly described elsewhere [17] was employed for the e.m.f. measurements. The oxygen potential at the two electrodes was fixed by flowing high-purity oxygen (99.99%) at a flow rate of 1 $dm^3\ h^{-1}$ and a pressure of $1.01 \times 10^5$ Pa over them. Prior to admission into the cell, the oxygen was passed through drierite (anhydrous $CaCl_2$) for the removal of traces of moisture present in the cylinder gas. The temperature of the cell was measured using a Pt–Pt/10%Rh thermocouple calibrated against the melting points of Sn, Bi, Zn, Sb and Ag. The head of the galvanic cell assembly was located in the isothermal zone of a non-inductively wound furnace. Temperature of the furnace was regulated by a proportional power controller to better than ±1 K. The reproducibility of the e.m.f. data was verified by thermal cycling and microcoulometric titration. Absence of asymmetric potential was checked by measuring near null e.m.f. with $Y_2O_3 + YF_3$ on either side of the solid electrolyte.

The reversible e.m.f. of the following cells were measured as a function of temperature

$$Pt, O_2, BaCuO_2, CuO, BaF_2|CaF_2|BaF_2, BaZrO_3, ZrO_2, O_2, Pt \quad (I)$$

$$Pt, O_2, Y_2O_3, YF_3|CaF_2|YF_3, Y_2Cu_2O_5, CuO, O_2, Pt \quad (II)$$

$$Pt, O_2, BaZrO_3, ZrO_2, BaF_2|CaF_2|BaF_2, Y_2BaCuO_5, Y_2Cu_2O_5, CuO, O_2, Pt \quad (III)$$

The cells are written such that the right-hand electrodes are positive.

TABLE I Summary of experimental conditions used for the synthesis of oxide compounds

| Starting mixture (molar ratio) | Temperature (K) | Durations of heat treatment (h) | Phases identified after heat treatment by X-ray diffraction |
|---|---|---|---|
| $BaCO_3 + ZrO_2$ (1:2) | 1273 | 24 + 24[a] | $BaZrO_3 + ZrO_2$ |
| $BaCO_3 + CuO$ (1:2) | (i) 1173<br>(ii) 1223 | 24<br>6 | $BaCuO_2 + CuO$ |
| $Y_2O_3 + CuO$ (1:2) | 1273 | 24 | $Y_2Cu_2O_5 + CuO$ |
| $Y_2O_3 + BaCO_3 + CuO$ (1:1:2) | 1273 | 36 + 24[a] | $Y_2BaCuO_5 + CuO$ |

[a] The pellets were ground after 24 h heat treatment, repelletized and heat treated for a further 24 h.

In these cells attainment of electrochemical equilibria were found to be rather sluggish and steady e.m.f. was realized only after a few hours. At lower temperatures, it took 8–24 h to establish equilibrium among various coexisting phases at the electrodes. Each of these cells were operated for a period of 7–10 days. In some cases, the discs of $CaF_2$ solid electrolyte were often found to have become opaque, presumably due to the finite solubility of oxygen in $CaF_2$ and precipitation of CaO. This opaque layer could, however, be easily removed by polishing the surfaces on the "Corosil" 600 paper until the transluscence was regained. After each e.m.f. run, the electrode pellets could be detached effortlessly indicating the absence of any reaction between the electrode and $CaF_2$ electrolyte.

The e.m.f. of Cells I, II and III are plotted in Figs 2–4. The e.m.f. is a linear function of temperature. The least squares regression analysis gives the following

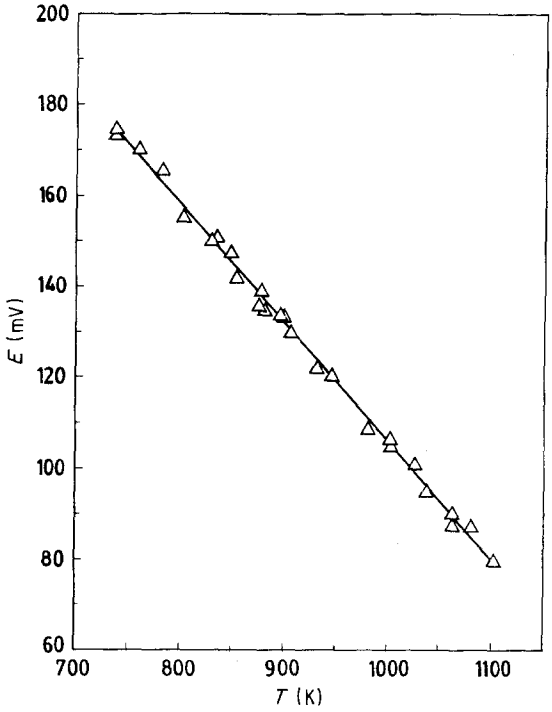


*Figure 2* Temperature dependence of e.m.f. of Cell I.

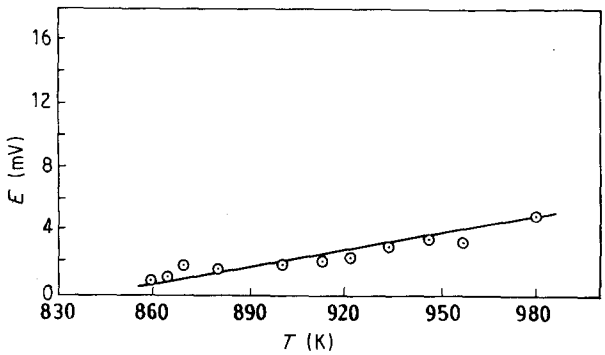


*Figure 3* Temperature dependence of e.m.f. of Cell II.

expressions for the e.m.f.

$$E_I(\pm 1.6)\,(\text{mV}) = 367.4 - 0.261199\,T(\text{K}) \quad (1)$$

in the temperature range 736–1102 K

$$E_{II}(\pm 0.5)\,(\text{mV}) = -31.9 + 0.037802\,T(\text{K}) \quad (2)$$

in the temperature range 861–980 K,

$$E_{III}(\pm 0.9)\,(\text{mV}) = -224.8 + 0.286507\,T(\text{K}) \quad (3)$$

in the temperature range 853–1066 K.

## 3. Discussion

### 3.1. The Gibbs' energy of formation of $BaCuO_2$

The two half-cell reactions in Cell I are

$$BaF_2 + ZrO_2 + \tfrac{1}{2}O_2 + 2e^- \rightarrow BaZrO_3 + 2F^- \quad (4)$$

$$2F^- + BaCuO_2 \rightarrow BaF_2 + CuO + \tfrac{1}{2}O_2 + 2e^- \quad (5)$$

For the passage of 2 F of electricity, the virtual cell reaction is

$$BaCuO_2 + ZrO_2 \rightarrow BaZrO_3 + CuO \quad (6)$$

The corresponding standard Gibbs' energy change ($\Delta G_R^0$) for Reaction 6, computed from the e.m.f. is

$$\Delta G_R^0(\pm 0.30)(\text{kJ}) = -70.9 + 0.050405\,T(\text{K}) \quad (7)$$

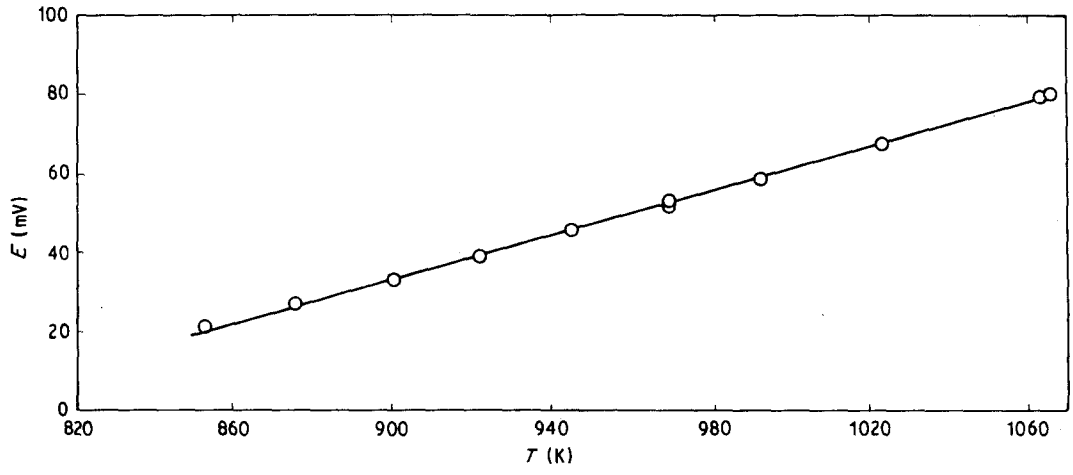


*Figure 4* Temperature dependence of e.m.f. of Cell III.

This is related to the standard Gibbs' energies of formation of $BaCuO_2$ and $BaZrO_3$ from the constituent binary oxides ($\Delta G^0_{f,ox}$) as

$$\Delta G^0_R = \Delta G^0_{f,ox}(BaZrO_3) - \Delta G^0_{f,ox}(BaCuO_2) \quad (8)$$

Levitskii [18] had reported data for the Gibbs' energy of formation of $BaZrO_3$

$$\Delta G^0_{f,ox}(BaZrO_3)(kJ\ mol^{-1}) = (-134.3 \pm 6.7) - (2.1 \pm 4.6) \times 10^{-3}\ T(K) \quad (9)$$

Combining Equations 7–9, the Gibbs' energy of formation of $BaCuO_2$ from component oxides in the temperature range 736–1102 K is obtained

$$\Delta G^0_{f,ox}(\pm 0.3)(kJ\ mol^{-1}) = -63.4 - 0.0525\ T(K) \quad (10)$$

It can be seen from Equation 10 that the entropy change, $\Delta S^0_{f,ox}$ for the solid reaction between BaO and CuO to form $BaCuO_2$ is rather high (52.5 $J\ K^{-1}\ mol^{-1}$). The error limit on $\Delta S^0_{f,ox}$ is estimated as $\pm$ 10 $J\ K^{-1}\ mol^{-1}$. The measured values correspond to a composition saturated with respect to CuO. In the absence of reliable information on the defect structure and nonstoichiometry of $BaCuO_2$, it is not possible at present to explain the high value for the entropy. Moreover, there are no data reported in the literature with which the present values of $\Delta G^0_{f,ox}$ of $BaCuO_2$ can be compared. Because of the limited temperature range covered in the study, the derived second law entropy is not likely to be very accurate. More accurate data on entropy must await calorimetric studies on $BaCuO_2$.

## 3.2. The Gibbs' energy of formation of $Y_2Cu_2O_5$

The two half-cell reactions in Cell II are

$$2YF_3 + 2CuO + 1.5O_2 + 6e^- \rightarrow Y_2Cu_2O_5 + 6F^- \quad (11)$$

$$Y_2O_3 + 6F^- \rightarrow 2YF_3 + 1.5\,O_2 + 6e^- \quad (12)$$

Thus for the passage of 6 F of electricity, the virtual cell reaction corresponding to Cell II is

$$Y_2O_3 + 2CuO \rightarrow Y_2Cu_2O_5 \quad (13)$$

The standard Gibbs' energy change ($\Delta G^0_R = -6$ F) for the reaction represented by Equation 13 is identical with the standard Gibbs' energy of formation of $Y_2Cu_2O_5$ from the constituent oxides. Hence from the e.m.f. of Cell II

$$\Delta G^0_{f,ox}(\pm 0.3)(kJ\ mol^{-1}) = 18.47 - 0.0219\ T(K) \quad (14)$$

Tretyakov *et al.* [16], Pankajavalli and Sreedharan [4] carried out e.m.f. measurements on oxide galvanic cells of the following configuration over the ranges 1173–1340 and 1097–1292 K, respectively:

$$Pt, Y_2O_3, Cu_2O, Y_2Cu_2O_5 \,|\, 15\ CSZ \,|\, air\ (p_{O_2} = 0.21 \times 10^5\ Pa), Pt \quad (IV)$$

Equations 15 and 16 were derived by Tretyakov *et al.* [16] and Pankajavalli and Sreedharan [4], respectively, for the Gibbs' energy of formation of $Y_2Cu_2O_5$ from oxides

$$\Delta G^0_{f,ox}(kJ\ mol^{-1}) = 21.24 - 0.022\,81\ T(K) \quad (15)$$

$$\Delta G^0_{f,ox}(kJ\ mol^{-1}) = 10.91 - 0.013\,41\ T(K) \quad (16)$$

Kale and Jacob [3] have proposed a phase diagram for the Cu–Y–O system, according to which $Cu_2O$, $Y_2O_3$ and $Y_2Cu_2O_5$ do not coexist at equilibrium. They have measured the oxygen potential corresponding to the three-phase field $YCuO_2 + Y_2Cu_2O_5 + Y_2O_3$ by an oxide-e.m.f. method over the range 873–1323 K. The Gibbs' energy of formation of $Y_2Cu_2O_5$ suggested by Kale and Jacob [3] is

$$\Delta G^0_{f,ox}(\pm 0.12)(kJ\ mol^{-1}) = 11.21 - 0.015\,07\ T(K) \quad (17)$$

Based on the assumption of a regular solution model, for the liquid phase and an incorrect phase diagram, Rao *et al.* [19] derived an expression for the Gibbs' energy of $Y_2Cu_2O_5$

$$\Delta G^0_{f,ox}(kJ\ mol^{-1}) = -59.21 + 0.029\,169\ T(K) \quad (18)$$

These measurements are compared in Fig. 5. The solid segments correspond to the actual temperature range of measurements in each investigation and the extrapolations are shown by broken lines. It can be seen from the figure that except for the estimate reported by Rao *et al.* [19], the other three sets of measurements are in fair agreement with the present investigation. The standard entropy of formation $\Delta S^0_{f,ox}$ for the solid reaction between $Y_2O_3$ and CuO obtained in this study (21.9 $J\ K^{-1}\ mol^{-1}$) is in good agreement with that reported by Tretyakov *et al.* (22.8 $J\ K^{-1}\ mol^{-1}$) and in qualitative agreement with those suggested by Kale and Jacob (15.1 $J\ K^{-1}\ mol^{-1}$) and Pankajavalli and Sreedharan (13.4 $J\ K^{-1}\ mol^{-1}$). However, the Gibbs' energies from the four experimental studies agree within $\pm$ 1 kJ.

The measured thermodynamic data for $Y_2Cu_2O_5$ suggest its disproportionation into $Y_2O_3$ and CuO at lower temperatures. The calculated decomposition temperatures are 931 K from the data of Tretyakov *et al.* [16], 814 K from the data of Pankajavalli and Sreedharan [4] and 744 K from the measurements of Kale and Jacob [3]. Because of the sluggish kinetics associated with the solid state reaction, the decomposition of $Y_2Cu_2O_5$ is not observed during differential thermal analysis (DTA).

## 3.3. The Gibbs' energy of formation of $Y_2BaCuO_5$

The two half-cell reactions in Cell III are

$$Y_2Cu_2O_5 + BaF_2 + \tfrac{1}{2}O_2 + 2e^- \rightarrow Y_2BaCuO_5 + CuO + 2F^- \quad (18)$$

$$BaZrO_3 + 2F^- \rightarrow BaF_2 + ZrO_2 + \tfrac{1}{2}O_2 + 2e^- \quad (19)$$

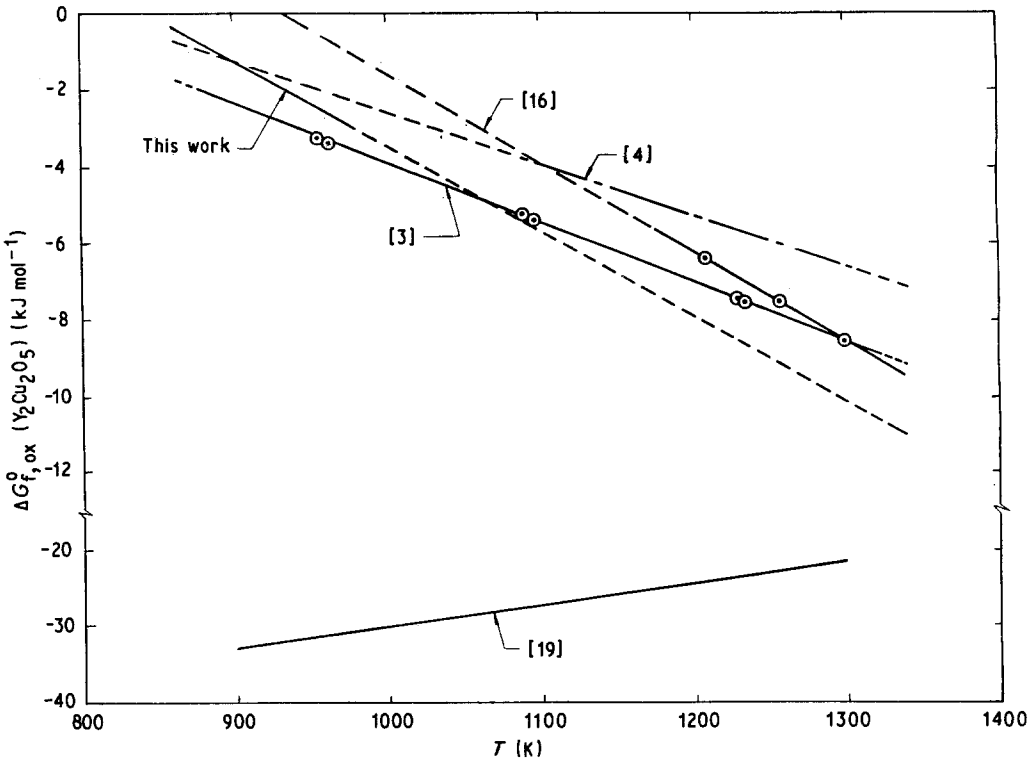


*Figure 5* Comparison of $\Delta G^0_{f,ox}$ of $Y_2Cu_2O_5$.

For the passage of 2 F of electricity, the virtual cell reaction is

$$Y_2Cu_2O_5 + BaZrO_3 \rightarrow Y_2BaCuO_5 + ZrO_2 + CuO \quad (20)$$

The Gibbs' energy change associated with this reaction, computed from the e.m.f. is

$$\Delta G^0_R(\pm 0.17)\,(kJ) = 43.4 - 0.055\,289\,T(K) \quad (21)$$

Further, the Gibbs' energy change for the cell reaction can be expressed in terms of Gibbs' energies of formation of $Y_2BaCuO_5$, $Y_2Cu_2O_5$ and $BaZrO_3$

$$\Delta G^0_R = \Delta G^0_{f,ox}(Y_2BaCuO_5) - \Delta G^0_{f,ox}(Y_2Cu_2O_5) - \Delta G^0_{f,ox}(BaZrO_3) \quad (22)$$

Now, there are four independent sets of data (as discussed in Section 3.2) on $\Delta G^0_{f,ox}$ of $Y_2Cu_2O_5$. In order to minimize the systematic errors, Equation 14 from the present study is used to compute the $\Delta G^0_{f,ox}$ of $Y_2BaCuO_5$. By combining Equation 22 with Equations 9, 14 and 21, an expression for Gibbs' energy of formation of $Y_2BaCuO_5$ from the component oxides $Y_2O_3$, BaO and CuO is obtained

$$\Delta G^0_{f,ox}(\pm 0.7)\,(kJ\,mol^{-1}) = -72.5 - 0.0793\,T(K) \quad (23)$$

in the temperature range 853–1066 K.

The only other report on the Gibbs' energy of formation of $Y_2BaCuO_5$ is by Pankajavalli and Sreedharan [6] who measured the oxygen potential corresponding to the three-phase mixture $Y_2BaCuO_5 + Y_2BaO_4 + Cu_2O$ in the temperature interval from 717–1021 K. The values of $-130.6$ kJ mol$^{-1}$ at 850 K and $-125.4$ kJ mol$^{-1}$ at 1050 K for $\Delta G^0_{f,ox}$ of $Y_2BaCuO_5$ from the work of Pankajavalli and Sreedharan [6] are in poor agreement with $-139.9$ and $-155.7$ kJ mol$^{-1}$ at the respective temperatures obtained in the present investigation. The positive value of 79.3 J K$^{-1}$ mol$^{-1}$ for $\Delta S^0_{f,ox}$ obtained in this work contrasts with the negative value of $-20$ J K$^{-1}$ mol$^{-1}$ suggested by Pankajavalli and Sreedharan [6].

## 4. Conclusion

The standard Gibbs' energies of formation of the compounds $BaCuO_2$, $Y_2Cu_2O_5$ and $Y_2BaCuO_5$ from component oxides were determined from the reversible e.m.f. of solid state cells based on $CaF_2$ under pure oxygen at a pressure of $1.01 \times 10^5$ Pa. These data provide a basis for evaluating the thermodynamic stability of 1–2–3 compound under identical conditions.


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## References


1. M. K. WU, J. R. ASHBURN, C. J. TORNG, P. H. HOR, R. L. MENG, L. GAO, Z. J. HUANG, Y. Q. WANG and C. W. CHU, *Phys. Rev. Lett.* **58** (1987) 908.
2. G. M. KALE and K. T. JACOB, *Solid State Ionics.* **34** (1989) 247.
3. *Idem., Mater. Chem.* **1** (1989) 515.

4. R. PANKAJAVALLI and O. M. SREEDHARAN, *J. Mater. Sci. Lett.* **7** (1988) 714.
5. A. M. AZAD and O. M. SREEDHARAN, *ibid.* **8** (1989) 67.
6. R. PANKAJAVALLI and O. M. SREEDHARAN, *ibid.* **8** (1989) 225.
7. *Idem., ibid.* **8** (1989) 697.
8. F. TOCI, A. SCHRUENKAMPER, M. CAMBINI and L. MANES, *Phys. C* **153/155** (1988) 838.
9. J. L. MacMANUS, D. J. FRAY and J. E. EVETTS, *Supercond. Sci. Technol.* **1** (1989) 291.
10. K. G. FRASE, E. G. LINIGER and D. A. CLARKE, *J. Amer. Ceram. Soc.* **70** (1987) C 204.
11. K. G. FRASE and D. A. CLARKE, *Adv. Ceram. Mater.* **2** (3B) (1987) 295 (special issue).
12. G. WANG, S.-J. WU, S. N. SONG, J. B. KETTERSON, L. D. MARKS, K. R. POEPPELMEIER and T. D. MASON, *ibid.* **2** (3B) (1987) 313.
13. R. S. ROTH, K. L. DAVIS and J. R. DENNIS, *ibid.* **2** (3B) (1987) 303.
14. D. M. DE LEEUW, C. A. H. A. MUTSAERS, C. LANGERIES, H. C. A. SMOORENBURG and P. J. ROMMERS, *Phys. C* **152** (1988) 39.
15. K. T. JACOB and Y. WASEDA, private communication.
16. Yu. D. TRETYAKOV, A. R. KAUL and N. V. MAKUKHIN, *J. Solid State Chem.* **17** (1976) 183.
17. A. M. AZAD and O. M. SREEDHARAN, *J. Appl. Electrochem.* **17** (1987) 949.
18. V. A. LEVITSKII, *J. Solid State Chem.* **25** (1978) 9.
19. G. H. RAO, J. K. LIANG and Z. Y. QIAO, *J. Less-Common Metals* **144** (1988) 215.

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