

Gibbs' energy of formation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (tetragonal)

A M AZAD, O M SREEDHARAN* and K T JACOB†

Metallurgy Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India

†Department of Metallurgy, Indian Institute of Science, Bangalore 560 012, India

Abstract. The high temperature ceramic oxide superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (1–2–3 compound) is generally synthesized in an oxygen-rich environment. Hence any method for determining its thermodynamic stability should operate at a high oxygen partial pressure. A solid-state cell incorporating CaF_2 as the electrolyte and functioning under pure oxygen at a pressure of 1.01×10^5 Pa has been employed for the determination of the Gibbs' energy of formation of the 1–2–3 compound. The configuration of the galvanic cell can be represented by:

Pt, O_2 , $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, Y_2BaCuO_5 , CuO , $\text{BaF}_2/\text{CaF}_2/\text{BaF}_2$, BaZrO_3 , ZrO_2 , O_2 , Pt.

Using the values of the standard Gibbs' energy of formation of the compounds BaZrO_3 and Y_2BaCuO_5 from the literature, the Gibbs' energy of formation of the 1–2–3 compound from the constituent binary oxides has been computed at different temperatures. The value of x at each temperature is determined by the oxygen partial pressure. At 1023 K for O content of 6.5 the Gibbs' energy of formation of the 1–2–3 compound is $-261.7 \text{ kJ mol}^{-1}$.

Keywords. Gibbs' energy; oxygen partial pressure; free energy; stability.

1. Introduction

The high temperature ceramic superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (1–2–3 compound) is generally synthesized in an oxygen-rich environment. Hence any method of determining its thermodynamic stability should operate at a high oxygen partial pressure. Kale and Jacob (1989a) and Azad *et al* (1991) have demonstrated the application of fluorine concentration cells for the determination of standard Gibbs' energy mixed oxides in the system $\text{YO}_{1.5}$ – BaO – CuO , under pure oxygen at a pressure of 1.01×10^5 Pa. This paper reports the determination of the standard Gibbs' energy of formation of 1–2–3 compound (from the constituent binary oxides) over the range 993 to 1179 K, using a solid-state galvanic cell incorporating single-crystal CaF_2 as the electrolyte.

2. Experimental

The $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ compound used in this investigation was prepared by citrate combustion and subsequent oxygen annealing as described elsewhere (Pankajavalli *et al* 1988). The superconducting oxide was characterized by XRD, T_c and magnetic susceptibility measurements. It was found to be a pure single-phase material, with a sharp T_c of 92 K, having a half width less than 2 K. The oxygen content was found to be 6.93 by iodometry, employing NaCuO_2 as the standard (Janaki 1988). The compounds

*For correspondence

Y_2BaCuO_5 and BaZrO_3 were prepared by the standard solid-state reaction route and characterized by XRD (Azad *et al* 1989). The 1-2-3 compound, Y_2BaCuO_5 , CuO and BaF_2 were mixed in equal weight ratio and compacted at a pressure of 100 MPa into a cylindrical pellet of 10 mm diameter and 2-3 mm thickness. The pellet was used as an electrode. The reference electrode was made from a mixture of BaZrO_3 , ZrO_2 and BaF_2 taken in the weight ratio 1:1:1. The mixture was then compacted into a cylindrical pellet. Cylindrical discs of single crystal CaF_2 of 10 mm diameter and 3 mm thickness (Harshaw Chemical Co., USA) served as the electrolyte.

An open-cell stacked-pellet assembly was used for emf measurements. The cell assembly was held in the constant temperature zone of the furnace. A calibrated Pt-10% Rh/Pt thermocouple, located in the vicinity of the stacked pellet assembly, was used to monitor the cell temperature. High purity oxygen (IOL, India, better than 99.99%), flowing at a rate of $\sim 1 \text{ dm}^3 \text{ h}^{-1}$ and a pressure of $1.01 \times 10^5 \text{ Pa}$ was used as the gas atmosphere over the cell. The oxygen was passed through drierite (anhydrous CaCl_2) traps for the removal of moisture prior to use in the cell. The other experimental details were identical to those reported earlier (Azad and Sreedharan 1987; Azad *et al* 1987, 1989). The following cell configuration was employed in the present study:

Pt, O_2 , $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, Y_2BaCuO_5 , CuO, $\text{BaF}_2/\text{CaF}_2/\text{BaF}_2$, BaZrO_3 , ZrO_2 , O_2 , Pt.

I

3. Results

The emf of cell I is shown in figure 1 for temperatures ranging from 993 to 1179 K. The least-square regression analysis gives the expression:

$$E (\pm 0.5)/\text{mV} = 93.8 - 0.02468 \text{ T/K}. \quad (1)$$

The cell voltages were measured over a much wider range (770 to 1180 K). The voltages above 1180 K were irreproducible, while those below 990 K exhibited an unacceptably large temperature dependence, presumably due to the non-attainment of equilibrium. The reproducibility of the emf was verified by thermal cycling and microcoulometric titration.

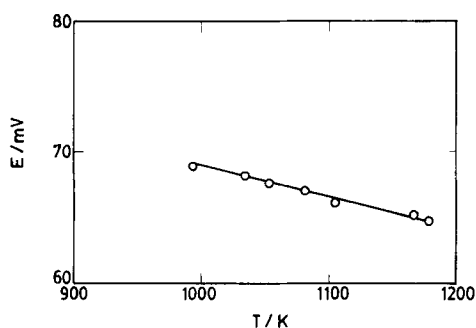
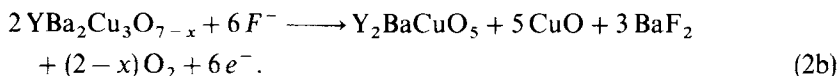
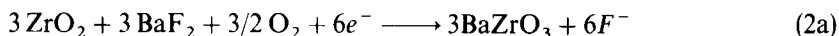


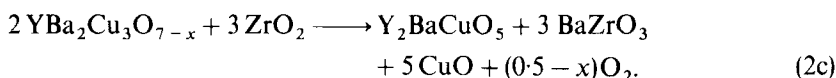
Figure 1. Temperature dependence of the emf of cell I.

4. Discussion

The half-cell reactions corresponding to cell I can be written as:



The overall virtual cell reaction is:



The standard Gibbs' energy change (ΔG_R°) for the virtual cell reaction, calculated from the emf, is given by:

$$\Delta G_{R(2)}^\circ (\pm 0.3)/\text{kJ} = -54.3 + 0.01429 \text{ T/K} \quad (3)$$

This is related to the standard Gibbs' energies of formation of various compounds in (2) by the expression:

$$\Delta G_{R(2)}^\circ = \Delta G_f^\circ(\text{Y}_2\text{BaCuO}_5) + 3\Delta G_f^\circ(\text{BaZrO}_3) + 5\Delta G_f^\circ(\text{CuO}) \\ - 3\Delta G_f^\circ(\text{ZrO}_2) - 2\Delta G_f^\circ(\text{YBa}_2\text{Cu}_3\text{O}_{7-x}) \quad (4)$$

The standard Gibbs' energy of formation of the ternary or quaternary oxides from the constituent binary oxides in their respective standard states may be represented by $\Delta G_{f,\text{ox}}^\circ$. In the case of the nonstoichiometric 1-2-3 compound, this can be done only at a temperature where O content is 6.5. Thus when the nonstoichiometric parameter x has a value of 0.5, (4) can be rewritten as:

$$\Delta G_{R(2)}^\circ = \Delta G_{f,\text{ox}}^\circ(\text{Y}_2\text{BaCuO}_5) + 3\Delta G_{f,\text{ox}}^\circ(\text{BaZrO}_3) \\ - 2\Delta G_{f,\text{ox}}^\circ(\text{YBa}_2\text{Cu}_3\text{O}_{6.5}) \quad (5)$$

Levitskii (1978) has determined the $\Delta G_{f,\text{ox}}^\circ$ for BaZrO_3 by using a similar galvanic cell with CaF_2 as the electrolyte:

$$\Delta G_{f,\text{ox}}^\circ/\text{kJ mol}^{-1} = (-134.3 \pm 6.7) - (2.1 \pm 4.6) \times 10^{-3} \text{ T/K} \quad (6)$$

Azad *et al* (1991) recently reported values for $\Delta G_{f,\text{ox}}^\circ$ of Y_2BaCuO_5 over the range 853 to 1066 K:

$$\Delta G_{f,\text{ox}}^\circ (\pm 0.7)/\text{kJ mol}^{-1} = -72.5 - 0.0793 \text{ T/K} \quad (7)$$

Rearrangement of (5) yields:

$$\Delta G_{f,\text{ox}}^\circ(\text{YBa}_2\text{Cu}_3\text{O}_{6.5}) = 0.5[\Delta G_{f,\text{ox}}^\circ(\text{Y}_2\text{BaCuO}_5) + 3\Delta G_{f,\text{ox}}^\circ(\text{BaZrO}_3) \\ - \Delta G_{R(2)}^\circ] \quad (8)$$

A general expression for the standard Gibbs' energy of formation of the 1-2-3 compound from the constituent binary oxides and gaseous oxygen, in the temperature range 993 to 1179 K can be written as:

$$\Delta G_f^\circ(\text{YBa}_2\text{Cu}_3\text{O}_{7-x})/\text{kJ mol}^{-1} = -210.6 - 0.04993 \text{ T/K} \quad (9)$$

The experimentally measured values of ΔG_f° of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, at O_{7-x} , different temperatures and the corresponding values of x are shown in table 1. Since the

Table 1. Standard Gibbs' energy of formation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ as a function of temperature and nonstoichiometry.

T(K)	E(mV)	x^a	$\Delta G_f^\circ(\text{YBa}_2\text{Cu}_3\text{O}_{7-x})/\text{kJ mol}^{-1}$
993.4	68.9	0.451	-260.2
1034.0	68.3	0.508	-262.2
1053.0	67.5	0.532	-263.2
1080.9	67.0	0.566	-264.6
1104.9	65.9	0.592	-265.8
1167.0	65.0	0.656	-268.9
1179.3	64.6	0.667	-269.5

^aderived from the work of Kishio *et al* (1989)

value of x varies with temperature, the temperature-independent term in (9) cannot be identified as the enthalpy of formation.

It is well known that the 1-2-3 compound exhibits an orthorhombic-to-tetragonal transition at high temperature which is dependent on the partial pressure of oxygen. Typically a value of 6.5 has been found to be the upper limit of O/M ($x = 0.5$) for the orthorhombic-to-tetragonal phase transition in pure oxygen at a pressure of 1.01×10^5 Pa (Schuller *et al* 1987; Murphey *et al* 1987). Many investigators (Gallagher 1987; Blinovskov *et al* 1988; Swaminathan *et al* 1988; Musbah and Chang 1989; O'Bryan *et al* 1989; Kishio *et al* 1989) have studied the dependence of the O/M ratio in the 1-2-3 compound on temperature and partial pressure of oxygen. Unfortunately there is very poor consistency among these measurements, either because the solid samples were not single phase or because equilibrium conditions were difficult to reach at low p_{O_2} and moderate temperatures. From the x - p_{O_2} relation reported by Kishio *et al* (1989), it is seen that in the temperature range of the present investigation, the 1-2-3 phase would exist mainly in the tetragonal modification. Thus combining (6) and (7) with (3), the $\Delta G_{f,ox}^\circ$ of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ at 1023 K was calculated to be -261.7 kJ mol⁻¹. This result can be combined with the data on the variation of oxygen partial pressure with nonstoichiometric parameter x to calculate the Gibbs' energies of formation at other compositions as a function of temperature. Morss *et al* (1988) determined the standard enthalpy of formation of $\text{YBa}_2\text{Cu}_3\text{O}_y$ ($y = 6.25, 6.47, 6.69$ and 6.93) at 298.15 K by solution calorimetry. They have reported a value of -143 kJ mol⁻¹ at 298.15 K for $\Delta H_{f,ox}^\circ(\text{YBa}_2\text{Cu}_3\text{O}_{6.5})$. On the other hand, Tretyakov and Graboy (1990), from their emf studies envisaged that the 1-2-3 compound is unstable and decomposes to BaCuO_2 , Y_2BaCuO_5 and CuO at temperatures below 973 K. This observation contradicts the large enthalpy of formation reported by Morss *et al* (1988) and the Gibbs' energy of formation obtained in the present investigation.

Acknowledgements

The authors are grateful to Dr P Rodriguez, Head, Metallurgy and Materials Programme and Shri J B Gnanamoorthy, Head, Metallurgy Division, for their keen interest and constant encouragement during the course of this collaborative effort.

References

- Azad A M, Sreedharan O M and Gnanamoorthy J B 1987 *J. Nucl. Mater.* **144** 91
- Azad A M and Sreedharan O M 1987 *J. Appl. Electrochem.* **17** 949
- Azad A M, Sreedharan O M and Jacob K T 1991 *J. Mater. Sci.* (in press)
- Blinovskov Ya N *et al* 1988 *Komi Scientific Centre and Sverdlovk Scientific Centre of the Ural Branch, USSR Academy of Science* **9** 24
- Gallagher P K 1987 *Adv. Ceram. Mater.* **2** 632
- Janaki J 1988 (private communication)
- Kale G M and Jacob K T 1989a *Solid State Ionics* **34** 247
- Kale G M and Jacob K T 1989b *Mater. Chem.* **1** 515
- Kishio K, Suzuki K, Hasegawa T, Yamamoto T and Kitazawa K 1989 *J. Solid State Chem.* **82** 192
- Levitskii V A 1978 *J. Solid State Chem.* **25** 9
- Morss L R, Sonnenberger D C and Thorn R J 1988 *Inorg. Chem.* **27** 2106
- Murphey D W, Sunshine S A, Gallagher P K, O'Bryan H M, Cava R J, Batlogg B, Dover R B, Schneemeyer L F and Zahurak S M 1987 in *Chemistry of high-temperature superconductors*, (eds.) D L Nelson, M S Whittingham and T F George Washington DC, *ACS Symp. Series* **351** 25
- Musbah O A and Chang Y A 1989 *Z. Metallkde* **80** 74
- O'Bryan H M, Gallagher P K, Laudise R A, Caporaso A J and Sherwood R C 1989 *J. Am. Ceram. Soc.* **72** 1298
- Pankajavalli R, Janaki J, Sreedharan O M, Gnanamoorthy J B, Rao G V N, Sankara Sastry V, Janawadkar M P, Hariharan Y and Radhakrishnan T S 1988 *Physica* **C156** 737
- Schuller I K, Hinks D G, Beno M A, Capone II D W, Soderholm L, Locquet J P, Bruynseraede Y, Segre C U and Zhang K 1987 *Solid State Commun.* **63** 385
- Swaminathan K, Janaki J, Rao G V N, Sreedharan O M and Radhakrishnan T S 1988 *Mater. Lett.* **6** 261
- Tretyakov Yu D and Graboy I E 1990 *Proc. Int. Conf. on superconductivity-ICSC*, Bangalore, India (eds) S K Joshi, C N R Rao and S V Subramanyam (Singapore: World Scientific) p. 121