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Thermodynamic stabilities of ternary oxides in Bi–Cu–O system by solid electrolyte EMF method

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Abstract

There are four high T_c compounds in the Bi–Sr–Ca–Cu–O system, the thermodynamic characterization of which may require precise Gibbs energy data on ternary compounds in different subsystems. Hence, phase equilibrium studies have been carried out on the less known Bi_2O_3 – Cu_2O – CuO system and a partial isothermal phase diagram has been determined at 973 K. Based on these equilibrium studies, three galvanic cells based on stabilized zirconia as the electrolyte and one galvanic cell based on single crystal CaF_2 as the electrolyte have been studied in the temperature range 650–950 K. From the EMF results, the following least-squares expressions for the standard Gibbs energy of formation of ternary oxides, $\Delta G_{f,\text{ox}}^\circ$ from their constituent binary oxides have been derived.

$$\Delta G_{f,\text{ox}}^\circ(\text{Bi}_5\text{CuO}_8) = -17\,390 + 11.62T \pm 200 \text{ J mol}^{-1} \quad (1)$$

$$\Delta G_{f,\text{ox}}^\circ(\text{Bi}_4\text{CuO}_7) = -24\,790 - 6.64T \pm 470 \text{ J mol}^{-1} \quad (2)$$

$$\Delta G_{f,\text{ox}}^\circ(\text{Bi}_2\text{CuO}_4) = -35\,040 + 11.89T \pm 570 \text{ J mol}^{-1} \quad (3)$$

$$\Delta G_{f,\text{ox}}^\circ(\text{Bi}_2\text{Cu}_2\text{O}_5) = -55\,210 + 20.15T \pm 830 \text{ J mol}^{-1} \quad (4)$$

The expressions for $\log P_{\text{O}_2}$ and $\log a_{\text{CuO}}$ over the relevant mixture of phases have also been derived and reported.

Keywords: Gibbs energy; EMF; Phase equilibrium; Solid electrolytes

1. Introduction

There are four superconducting phases with high T_c in the Bi–Sr–Ca–Cu–O system designated as Bi-1212 (with yttrium doping) [1], 2201, 2212 and 2223 [2–4]. Extensive work on the synthesis of these superconducting phases through condensed state reactions is being reported in the literature [5–8] with somewhat limited information on partial phase diagrams and stability ranges of impurity phases [9–11]. Reliable thermodynamic data on the formation reactions of ternary oxides in this system would considerably assist in formulating pathways for the synthesis of pure high T_c phases. The phase diagram of the subsystem Sr–Cu–O in air has been reported by several investigators [12–15]. This has facilitated the determination of the standard Gibbs energy of formation, ΔG_f° of some ternary oxides in the Sr–Cu–O system by Alcock and Li [16] and Suzuki et al. [15] employing the solid electrolyte EMF

method. The phase equilibria in Ca–Cu–O and Bi–Sr–O systems have been studied by Roth et al. [17] and Abbattista et al. [18], respectively. So far no authentic phase diagram of the Bi–Cu–O system has been reported, but several attempts have been made to determine partial phase diagrams of this system [19–24]. Many contradictory observations on the existence of some of the ternary oxides and their thermal stabilities have been found in these reports, which warrant a re-examination of the relevant phase equilibria. Further, the magnetic properties of the compound, Bi_2CuO_4 have been of considerable interest in materials science [25–28]. Mixed oxide composites of the Bi–Cu–O system have been used as cathodes in organic electrolyte batteries and also as piezo-electric transducers [29–31]. Hence, determination of the thermodynamic stabilities of the oxide phases in the Bi_2O_3 – Cu_2O – CuO system would be useful not only for the synthesis of superconducting phases but also from the view point of materials science as a whole. Therefore, in this work the standard Gibbs energy data for the formation of

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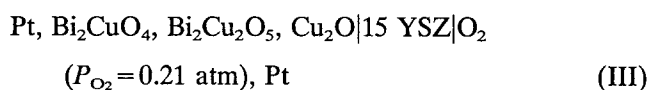
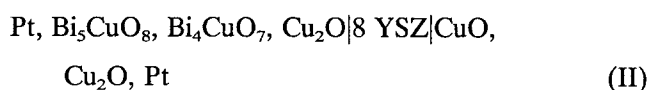
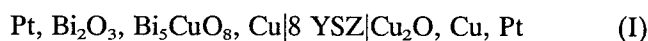
the oxide phases Bi_4CuO_7 , Bi_2CuO_4 and $\text{Bi}_2\text{Cu}_2\text{O}_5$ in the pseudo binary Bi_2O_3 – CuO system and on the formation of Bi_5CuO_8 in the system Bi_2O_3 – Cu_2O have been reported by the solid electrolyte EMF technique after ascertaining the relevant co-existing phases.

2. Experimental procedure

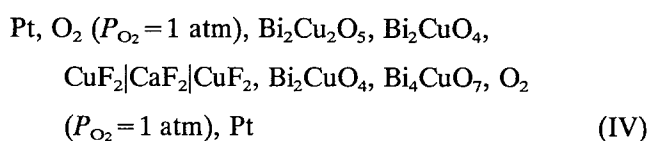
The starting materials were high purity (better than 99.9%) Bi_2O_3 (Johnson-Matthey Chemicals, UK), electrolytic Cu powder (Spex Industries, Inc., USA), CuO (Loba-Chemie, India) and CuF_2 (Koch-Light, UK). Cuprous oxide, Cu_2O was produced by thermal decomposition of CuO in a stream of purified argon at 1323 K for 4–6 h. The compounds Bi_4CuO_7 , Bi_2CuO_4 and $\text{Bi}_2\text{Cu}_2\text{O}_5$ were synthesized using the solid-state route by intimate blending of mixtures of Bi_2O_3 and CuO in appropriate mole ratios followed by compaction into cylindrical pellets of diameter 10 mm and thickness 2–3 mm at a compacting pressure of 100 MPa. These pellets were heated in air at 773 K for 24 h, at 823 K for 10 h and at 973 K for 48 h. The last step of heating at 973 K was repeated twice after grinding and compacting the materials each time in order to ensure completion of the reaction as confirmed by powder X-ray diffractometry (XRD) within its 5 mass% limit of detection of impurity phases. The procedure for the synthesis of Bi_5CuO_8 was identical to the above, except that the starting materials were Bi_2O_3 and Cu_2O (in the mole ratio 5:1) and the heat treatment was done after sealing the pellets in evacuated silica ampoules. The electrode pellets were prepared similarly from phases indicated in the cell configurations given below and compacting the powders as described earlier for the synthesis of compounds. Prior to the use of the electrode pellets in the EMF measurements, a representative sample of each batch of pellets was heated in purified argon at a minimum flow rate at a temperature of 973 K for about 24 h and after cooling to room temperature in the same atmosphere, the co-existence of the phases was confirmed by XRD. In the case of an electrode containing copper, the phase analysis was carried out after heating the pellet in evacuated and sealed silica ampoules under identical conditions of temperature and duration. Three types of electrolytes were used in the EMF measurements described below. In the open-cell-stacked pellet assembly (for cells (I) and (II)), oxide electrolyte cups made of 8 wt.% Y_2O_3 -stabilized ZrO_2 (8 YSZ, Nippon Kagaku Togyo Co. Ltd., Japan) with the dimensions 10 mm outer diameter, 7 mm inner diameter and 5 mm depth and a flat bottom, were employed. A cylindrical solid electrolyte tube with one end closed and the closed end flat, having a composition of 15 wt.% Y_2O_3 -stabilized ZrO_2 (15 YSZ, Corning, USA) with dimensions of 12.7 mm outer

diameter, 9.8 mm inner diameter and length 300 mm, was used for the galvanic cell (III). Single crystal CaF_2 cylindrical discs (Harshaw/Filtrol, USA) of dimensions 10 mm in diameter and 3 mm thickness were used as an electrolyte in the galvanic cell (IV).

The following galvanic cells were assembled and studied:



and



The reproducibility of the measured EMF had been ascertained by a 10% variation in the ratio of the co-existing phases in each electrode from one run to another. In addition, the usual tests for reversibility of the galvanic cell voltages such as the repeatability of the EMF values in different thermal cyclings and on micropolarization were carried out. A purified helium atmosphere was employed in cells (I) to (III), while high purity oxygen at unit fugacity had been used for cell (IV). The precautions with respect to measurement of temperature in the uniform temperature zone with a calibrated Pt–10% Rh/Pt thermocouple and elimination of asymmetric potentials in EMF measurements were the same as described elsewhere [32–35]. The electrodes were examined by XRD after each experimental run in order to confirm the absence of changes in phase composition.

3. Results and discussion

3.1. Phase equilibrium studies

The coexistence of Cu, Bi_5CuO_8 and Bi_2O_3 has been confirmed by the phase equilibrium studies. The tie lines between the pairs of phases $\text{Bi}_4\text{CuO}_7/\text{Bi}_2\text{CuO}_4$ and $\text{Bi}_2\text{CuO}_4/\text{Bi}_2\text{Cu}_2\text{O}_5$ have been confirmed by phase equilibration at 973 K. In addition, two more ternary oxides richer in CuO, namely $\text{Bi}_2\text{Cu}_6\text{O}_9$ and $\text{Bi}_2\text{Cu}_8\text{O}_{11}$, have also been reported in the literature [29,36], but no attempt is made here even to verify the existence of these phases for reasons discussed in a later section. The co-existence of $\text{Bi}_5\text{CuO}_8/\text{Bi}_4\text{CuO}_7/\text{Cu}_2\text{O}$ has also been established prior to the EMF studies. There is

considerable controversy in the literature even on the pseudo-binary phase diagram of the system $\text{Bi}_2\text{O}_3\text{--CuO}$ determined in air over the temperature range 773–1300 K [19–22,24,27]. For instance, Bi_2CuO_4 is reported to melt congruently at 1113 K by Boivin et al. [27] and at 1123 K by Kakhan et al. [20], while Kargin and Skorikov [21] have reported the melting to be incongruent at 1148 K. Incongruent melting of the same compound has also been reported by Kulakov and Lenchenko [24] at 1113 K at which temperature the sample starts losing oxygen, followed by completion of melting at 1158 K. According to Edwards [22], the compound Bi_4CuO_7 does not exist and Bi_2CuO_4 is the only stable ternary oxide in the system $\text{Bi}_2\text{O}_3\text{--CuO}$ presumably between 1050 and 1110 K. However, Casedanne and Campelo [19] have reported that the compound Bi_4CuO_7 decomposes peritectically at 1093 K and has a eutectic at 873 K with a melt containing 90 mol% Bi_2O_3 . Arjomand and Machin [37] have synthesized $\text{Bi}_2\text{Cu}_2\text{O}_5$ which has also been reported earlier by Murenkov et al. [36]. The foregoing discussion (which shows the existence of contradictory observations on the stability of ternary phases in the $\text{Bi}_2\text{O}_3\text{--CuO}$ system) could be reasonably resolved in the context of the present studies.

Dynamic techniques such as the DTA might reveal only that phase(s) whose formation is kinetically favoured. This may be responsible for the identification of Bi_2CuO_4 as the only stable phase in the $\text{Bi}_2\text{O}_3\text{--CuO}$ system by other investigators [20–22,24,27], mainly employing the DTA technique. It is known that CuO would lose oxygen in air only above 1300 K [38]. Hence, it is difficult to understand the loss of weight by nearly stoichiometric Bi_2CuO_4 in air below this temperature as observed by Edwards [22] and Kulakov and Lenchenko [24]. Other phases, namely Bi_4CuO_7 and $\text{Bi}_2\text{Cu}_2\text{O}_5$, are found to require long duration of heating at 973 K in order to facilitate their formation in the present studies. The isothermal cross-section of the partial phase diagram of $\text{Bi}_2\text{O}_3\text{--Cu}_2\text{O--CuO}$ system at 973 K arrived at as a result of these studies is given in Fig. 1.

3.2. EMF results and evaluation of standard Gibbs energy data

The EMF results on cell (I) given in Table 1 are plotted in Fig. 2 as a function of temperature. The data could be fitted into the following least-squares expression valid over the temperature range 701–941 K.

$$E_{(1)} = 180.21 - 0.12042T \pm 1.99 \text{ mV} \quad (1)$$

For the passage of 1 Faraday of electricity, the half cell reactions for cell (I) could be represented as

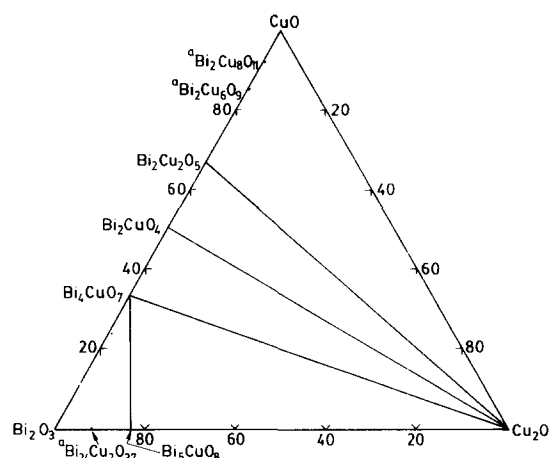


Fig. 1. Partial phase equilibrium diagram of the system $\text{Bi}_2\text{O}_3\text{--Cu}_2\text{O--CuO}$ at 973 K. *Existence not confirmed.

Table 1
Measured EMF results for cell (I)

Run	<i>T</i> (K)	<i>E</i> (mV)	<i>T</i> (K)	<i>E</i> (mV)	<i>T</i> (K)	<i>E</i> (mV)
1	725.1	91.02	806.9	80.32	869.9	78.91
	789.3	85.06	856.3	74.13	926.7	69.98
	748.5	91.83	821.7	83.39		
2	725.3	92.61	797.5	86.82	815.0	80.12
	941.4	67.83	700.6	95.16		
3	757.2	90.31	831.9	80.86	909.9	69.92
	847.1	81.18	894.9	69.95	732.7	91.27
	927.5	65.73				

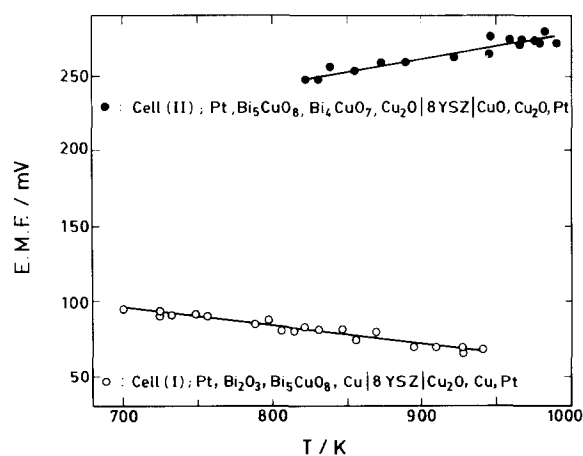
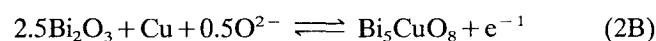
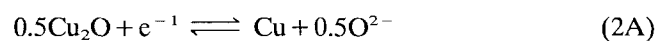
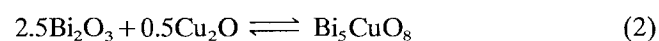


Fig. 2. Experimental EMF results of cells (I) and (II).



Combining (2A) and (2B), the overall cell reaction leads to the following:



Using the Nernst equation, the standard Gibbs energy change, ΔG_r° for the reaction (2) is found to be

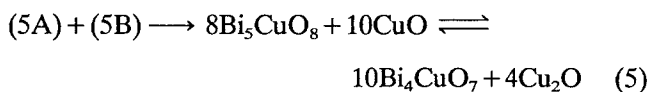
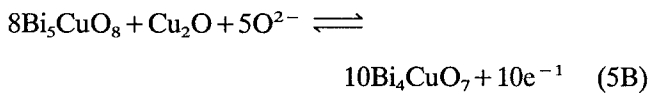
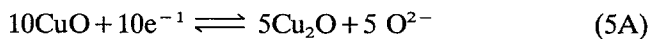
$$\Delta G_{r(2)}^\circ = \Delta G_{f,ox}^\circ(\text{Bi}_5\text{CuO}_8) \\ = -17\,390 + 11.62T \pm 200 \text{ J mol}^{-1} \quad (3)$$

The term, $\Delta G_{f,ox}^\circ$ in Eq. (3) stands for the standard Gibbs energy of formation of $\text{Bi}_5\text{CuO}_8(\text{s})$ from its constituent binary oxides. Since reaction (2) is a solid-solid reaction, one would expect the standard entropy of formation, $\Delta S_{f,ox}^\circ$ to be quite small (of the order of $+10 \text{ J mol}^{-1} \text{ K}^{-1}$). However, the slope of Eq. (3) gives a value of $-12 \text{ J mol}^{-1} \text{ K}^{-1}$ for $\Delta S_{f,ox}^\circ$ which, although negative, can be still considered as consistent by its small magnitude with what one expects for an all-condensed phase reaction.

The results of EMF runs for cell (II) given in Table 2 and also plotted in Fig. 2 could be fitted into the following least-squares expression valid over the range 822-989 K.

$$E_{(II)} = 112.73 + 0.16515T \pm 3.25 \text{ mV} \quad (4)$$

For the passage of 10 F of electricity, the half-cell reactions and the overall cell reaction for the galvanic cell (II) could be represented as given below.



The $\Delta G_{r(5)}^\circ$ for the reaction (5) is calculated from the EMF expression (4) to be

$$\Delta G_{r(5)}^\circ = -108\,800 - 159.35T \pm 3200 \text{ J mol}^{-1} \quad (6)$$

By appropriate combination of Eqs. (3) and (6) taking into account the cell reactions (2) and (5), the $\Delta G_{f,ox}^\circ$ of Bi_4CuO_7 has been determined and is given as

$$\Delta G_{f,ox}^\circ(\text{Bi}_4\text{CuO}_7) = -24\,790 - 6.64T \pm 470 \text{ J mol}^{-1} \quad (7)$$

Table 2
Experimental EMF results for cell (II)

Run	T (K)	E (mV)	T (K)	E (mV)	T (K)	E (mV)
1	839.1	255.13	920.6	261.85	958.5	273.54
	889.2	258.92	964.2	270.48		
2	872.8	258.72	944.8	264.81	822.4	247.57
	945.2	276.03				
3	855.2	252.68	965.9	273.62	978.4	271.54
	975.4	273.14	831.3	247.46	989.4	271.55
	981.3	279.89				

The value of $+7 \text{ J mol}^{-1} \text{ K}^{-1}$ for $\Delta S_{f,ox}^\circ$ is considered to be highly reasonable indicating that there is no significant change in the degree of order/disorder in the relevant condensed phase reaction.

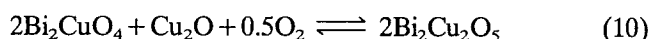
The stability of $\text{Bi}_2\text{Cu}_2\text{O}_5$ could be assessed from the EMF results on cell (III) represented in Table 3 and Fig. 3. The least-squares regression analysis of these data has yielded the expression

$$E_{(III)} = 885.04 - 0.60593T \pm 1.13 \text{ mV} \quad (8)$$

over the temperature range 772-950 K. After correcting for the standard state of oxygen in the reference air ($P_{\text{O}_2} = 0.21 \text{ atm}$)/Pt electrode, the ΔG_r° for the passage of 2 F of electricity has been calculated from Eq. (8) to be

$$\Delta G_r^\circ = -170\,800 + 110.43T \pm 220 \text{ J mol}^{-1} \quad (9)$$

which corresponds to the overall cell reaction



Substituting the value of ΔG_r° from Eq. (9) into reaction (10) along with the Gibbs energy data for the

Table 3
Measured results for cell (III): Pt, Bi_2CuO_4 , $\text{Bi}_2\text{Cu}_2\text{O}_5$, Cu_2O |15 YSZ| O_2 ($P_{\text{O}_2} = 0.21 \text{ atm}$), Pt

Run	T (K)	E (mV)	T (K)	E (mV)	T (K)	E (mV)
1	789.4	404.95	837.3	378.86	871.1	357.75
	903.4	337.43	935.7	317.59	771.9	417.19
	837.9	378.91	943.4	312.68	781.9	408.84
	866.3	360.43	915.0	329.98	899.2	340.42
	929.2	320.75				
2	820.3	387.77	853.7	368.55	886.6	347.51
	918.3	327.83	949.8	307.87	792.4	404.32
	825.2	386.42	859.8	365.91	891.6	345.56
	796.7	401.31	832.9	381.04	910.2	332.54
	814.2	391.77	926.2	323.23	881.1	351.28
3	808.8	395.34	841.8	376.45	877.1	355.46
	908.1	335.69	789.1	408.43	854.4	368.12
	895.2	343.03	800.0	399.15	776.6	412.35

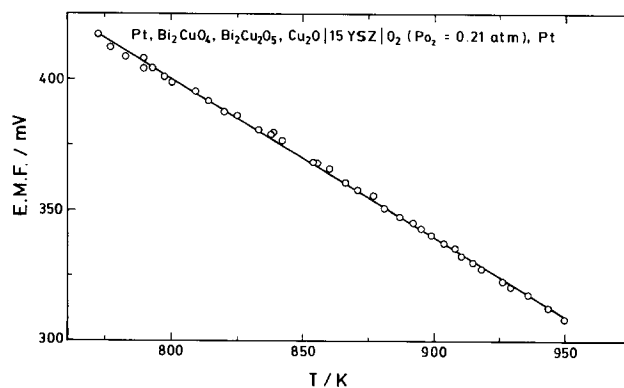
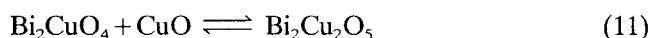


Fig. 3. Measured EMF as a function of temperature for cell (III).

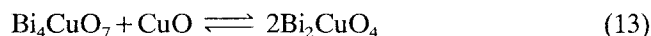
formation of Cu_2O from CuO [38], the ΔG_r° for the reaction



has been calculated and is given as follows:

$$\Delta G_{r(11)}^\circ = -20\,170 + 8.27T \pm 260 \text{ J mol}^{-1} \quad (12)$$

In order to determine the $\Delta G_{f,\text{ox}}^\circ$ of Bi_2CuO_4 , the ΔG_r° of the following reaction is required:



To evaluate $\Delta G_{r(13)}^\circ$, the EMF of cell (IV) has been measured over the temperature range 662–854 K. The results so obtained are summarized in Table 4 and Fig. 4 and by the least-squares expression

$$E_{(\text{IV})} = 130.15 - 0.11476T \pm 2.12 \text{ mV} \quad (14)$$

For the passage of 2 F of electricity, the half-cell reactions and the overall cell reaction of cell (IV) could be written as

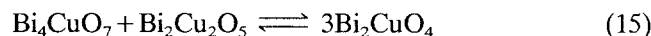
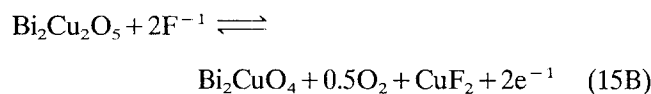
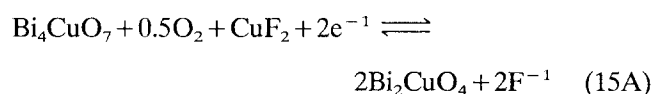


Table 4
Experimental EMF results for the fluoride cell (IV)

Run	<i>T</i> (K)	<i>E</i> (mV)	<i>T</i> (K)	<i>E</i> (mV)	<i>T</i> (K)	<i>E</i> (mV)
1	661.6	52.43	736.9	48.22	693.4	49.45
	831.1	37.52	751.3	42.01		
2	700.6	53.82	786.4	40.11	677.8	52.84
3	669.7	52.15	854.2	29.84	769.0	40.07

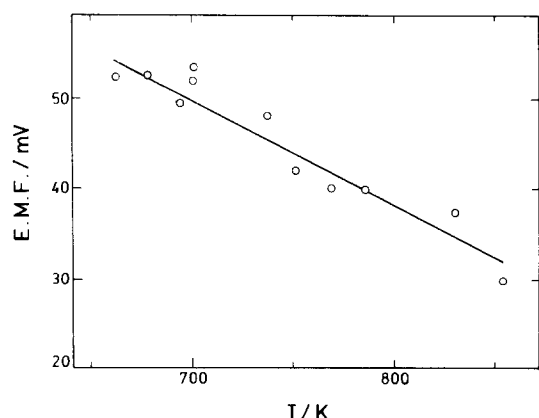


Fig. 4. Measured EMF results for cell (IV): Pt, O_2 (1 atm), Bi_2CuO_4 , $\text{Bi}_2\text{Cu}_2\text{O}_5$, $\text{CuF}_2|\text{CaF}_2|\text{CuF}_2$, Bi_2CuO_4 , Bi_4CuO_7 , O_2 (1 atm), Pt.

corresponding to $\Delta G_{r(15)}^\circ$ (derived from Eq. (14)).

$$\Delta G_{r(15)}^\circ = -25\,120 + 22.15T \pm 410 \text{ J mol}^{-1} \quad (16)$$

Adding the ΔG_r° values from Eqs. (12) and (16) corresponding to reactions (11) and (15), one obtains the ΔG_r° expression for reaction (13).

$$\Delta G_{r(13)}^\circ = -45\,290 + 30.41T \pm 670 \text{ J mol}^{-1} \quad (17)$$

Combining Eq. (7) with Eq. (17), one obtains

$$\Delta G_{f,\text{ox}}^\circ(\text{Bi}_2\text{CuO}_4) = -35\,040 + 11.89T \pm 570 \text{ J mol}^{-1} \quad (18)$$

Similarly by adding Eqs. (12) and (18), $\Delta G_{f,\text{ox}}^\circ$ of $\text{Bi}_2\text{Cu}_2\text{O}_5$ could be determined.

$$\Delta G_{f,\text{ox}}^\circ(\text{Bi}_2\text{Cu}_2\text{O}_5) = -55\,210 + 20.15T \pm 830 \text{ J mol}^{-1} \quad (19)$$

For checking the consistency of Gibbs energy data, the thermodynamic activity of CuO is calculated for the co-existing biphasic mixtures in the Bi_2O_3 – CuO system and is summarized in Table 5. It can be seen from this table that with increasing CuO content, the isothermal $\log a_{\text{CuO}}$ increases as expected. Values of $\log a_{\text{CuO}}$ computed at 973 K show that apart from Bi_2CuO_4 , $\text{Bi}_2\text{Cu}_2\text{O}_5$ is also a stable phase. However, the high value of $\log a_{\text{CuO}}$ is suggestive of even much lower driving force (CuO potential = $RT \ln a_{\text{CuO}}$) for the formation of higher CuO -containing phases such as $\text{Bi}_2\text{Cu}_6\text{O}_9$ (of the order of -10 kJ mol^{-1} or less). The EMF studies thus uphold the validity of the partial phase diagram given in Fig. 1.

The values of $\log P_{\text{O}_2}$ for some of the co-existing phase fields calculated from the Gibbs energy data have been summarized in Table 6. These values would be helpful in assessing the $\log P_{\text{O}_2}$ -temperature domain of stability of the ternary oxides in the Bi–Cu–O system. This information in conjunction with other three-component phase diagrams such as those of Ca–Cu–O and Bi–Sr–O might facilitate theoretical calculation of multicomponent phase diagrams to understand the metastability of the superconducting phases. The standard Gibbs energy data determined in the present investigation could be considered as summarized in the form of numerical expressions (3), (7), (18) and (19) for the $\Delta G_{f,\text{ox}}^\circ$ of the oxides Bi_5CuO_8 , Bi_4CuO_7 , Bi_2CuO_4 and $\text{Bi}_2\text{Cu}_2\text{O}_5$, respectively. The reasonably small magnitude of the temperature coefficients (except perhaps for a slightly larger value in Eq. (19)) in these equations are consistent with what one expects for solid-solid reactions. However, the intercepts and slopes of these expressions cannot be directly taken as $\Delta H_{f,\text{ox}}^\circ$ and $-\Delta S_{f,\text{ox}}^\circ$ unless independently assessed by a third-law evaluation [34,39]. According to Kubaschewski [40], the solid electrolyte EMF method yields very precise Gibbs energy data even though the derived enthalpy and entropy data may not be as reliable as Gibbs energy values without independent assessment. However, values of $S_{f,298}^\circ$ and C_p° data as a function of temperature are not known

Table 5
Activity of CuO in the biphasic regions of the Bi₂O₃–CuO system

Serial no.	Mixture	$\log a_{\text{CuO}} = A - B/T(\text{K})$	$\log a_{\text{CuO}}$ at 973 K	Equation no.
1	2 Bi ₂ O ₃ /Bi ₄ CuO ₇	$-0.35 - 1295/T \pm 0.03$	-1.68	(7)
2	Bi ₄ CuO ₇ /2 Bi ₂ CuO ₄	$1.59 - 2366/T \pm 0.04$	-0.84	(17)
3	Bi ₂ CuO ₄ /Bi ₂ Cu ₂ O ₅	$0.43 - 1054/T \pm 0.02$	-0.65	(12)

Table 6
Values of $\log P_{\text{O}_2}$ for some three phase fields in the Bi–Cu–O system

Serial no.	Co-existing mixture	$\log P_{\text{O}_2} (\text{atm}) = A - B/T(\text{K})$	$\log P_{\text{O}_2} (\text{atm})$ at 973 K
1	Bi ₂ O ₃ /Bi ₅ CuO ₈ /Cu	$9.88 - 21055/T$	-11.8
2	Bi ₅ CuO ₈ /Bi ₄ CuO ₇ /Cu ₂ O	$6.48 - 15902/T$	-9.9
3	Bi ₄ CuO ₇ /Bi ₂ CuO ₄ /Cu ₂ O	$16.17 - 23092/T$	-7.6
4	Bi ₂ CuO ₄ /Bi ₂ Cu ₂ O ₅ /Cu ₂ O	$11.54 - 17844/T$	-6.8

for any of these compounds to facilitate a third-law analysis. Under these circumstances, the first term in expressions (3), (7), (18) and (19) could be at best taken as $\Delta H_{f,\text{ox}}^\circ$ valid at a mean temperature, T_{mean} of each set of measurements namely at 821, 901, 861 and 758 K, respectively. Evaluation of $\Delta H_{f,\text{ox}}^\circ$ at 298 K from those determined at T_{mean} is therefore not feasible for the reasons stated here. Nevertheless, a comparison of the value of -35 kJ mol^{-1} at 861 K for $\Delta H_{f,\text{ox}}^\circ$ of Bi₂CuO₄ from Eq. (18) with $-13 \pm 3 \text{ kJ mol}^{-1}$ at 298 K reported by Idemoto et al. [41] using solution calorimetry shows that the agreement is rather poor. Other than this calorimetric work, there are no other values in the literature to assess the correctness of enthalpies.

The systematic increase in $\log a_{\text{CuO}}$ from one biphasic region to another with increasing mole fraction of CuO can be considered as indicative of the accuracy of the present measurements. This is because both oxygen and fluorine potential measurements have been combined to derive $\Delta G_{f,\text{ox}}^\circ$ of Bi₂CuO₄. Since the activity of CuO is expected to be higher than what has been determined in the case of Bi₂CuO₄/Bi₂Cu₂O₅ (e.g. $\log a_{\text{CuO}} = -0.65$ at 973 K for Bi₂CuO₄/Bi₂Cu₂O₅ mixture), no attempt is made either to characterize or to study the higher CuO bearing phases such as Bi₂Cu₆O₉ and Bi₂Cu₈O₁₁.

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