Combined Use of Oxide and Fluoride Solid Electrolytes for the Measurement of Gibbs Energy of Formation of Ternary Oxides: System Bi–Ca–O

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Phase equilibrium studies of the ternary system Bi–Ca–O at 1000 K and ambient pressure indicate that all the ternary oxides lie along the pseudo-binary line Bi_2O_3 –CaO. Four ternary oxides, $\text{Bi}_2\text{Ca}_2\text{O}_5$, $\text{Bi}_6\text{Ca}_4\text{O}_{13}$, Bi_2CaO_4 and $\text{Bi}_{14}\text{Ca}_5\text{O}_{26}$ and two phases of variable composition (δ and β) are identified. The chemical potential of CaO in two-phase fields of the pseudo-binary Bi_2O_3 –CaO is determined as a function of temperature using solid state cells based on single crystal CaF_2 as the electrolyte. The chemical potential of Bi_2O_3 in the two-phase fields is measured using cells incorporating $(\text{Y}_2\text{O}_3)\text{ZrO}_2$ as the solid electrolyte. The standard Gibbs free energy of formation of each ternary oxide from the binary oxides is calculated independently from the chemical potentials of CaO and Bi_2O_3 in two-phase fields on either side of the compound composition. The independent assessments agree closely; the maximum difference in the value of ΔG_f^0 ($\text{Bi}_{2m}\text{Ca}_n\text{O}_{3m+n}$)/ $(m+n)$ is 170 J/mol of the component binary oxides. The results are discussed in the light of the phase diagram and compared with calorimetric and free energy measurements reported in the literature. The combined use of emf data from cells incorporating fluoride and oxide electrolytes enhances the reliability of derived data. Free energies of formation of ternary oxides from component binary oxides are given by the following equations:

$$\begin{array}{ll} \text{Bi}_2\text{Ca}_2\text{O}_5: & \Delta G_{f,\text{ox}}^0 (\text{J/mol}) = -43800 + 5.79T (\pm 900) \\ \text{Bi}_6\text{Ca}_4\text{O}_{13}: & \Delta G_{f,\text{ox}}^0 (\text{J/mol}) = -109800 + 7.04T (\pm 2300) \\ \text{Bi}_2\text{CaO}_4: & \Delta G_{f,\text{ox}}^0 (\text{J/mol}) = -31910 + 2.31T (\pm 650) \\ \text{Bi}_{14}\text{Ca}_5\text{O}_{26}: & \Delta G_{f,\text{ox}}^0 (\text{J/mol}) = -184560 + 12.76T (\pm 4320) \\ \text{Bi}_{1.4}\text{Ca}_{0.3}\text{O}_{2.4} (\beta): & \Delta G_{f,\text{ox}}^0 (\text{J/mol}) = -12290 (\pm 300) \text{ at } 900 \text{ K} \\ \text{Bi}_{1.56}\text{Ca}_{0.22}\text{O}_{2.56} (\beta): & \Delta G_{f,\text{ox}}^0 (\text{J/mol}) = -9890 (\pm 180) \text{ at } 900 \text{ K} \end{array}$$

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I. Introduction

As a part of systematic studies on phase equilibria and thermodynamic properties of the quaternary system Bi–Ca–Sr–Cu–O which contains several superconducting oxides, measurements have been made on the ternary system Bi–Ca–O. High temperature Bi_2O_3 -based solid solutions are also of interest as electrolytes for solid oxide fuel cells.

The phase diagram for the pseudo-binary system Bi_2O_3 –CaO has been investigated by Conflant *et al.*⁽¹⁾, Burton *et al.*⁽²⁾ and Vstavskaya *et al.*⁽³⁾. Employing high temperature X-ray analysis (HTXRD) and differential thermal analysis (DTA), Conflant *et al.*⁽¹⁾ identified four compounds, $\text{Bi}_{14}\text{Ca}_5\text{O}_{26}$, Bi_2CaO_4 , $\text{Bi}_{10}\text{Ca}_7\text{O}_{22}$ and $\text{Bi}_6\text{Ca}_7\text{O}_{16}$, and three solid solutions (δ , fcc; γ , bcc; β_1/β_2 , rhombohedral). All four compounds decompose in the solid state before melting. Additional XRD data on the stoichiometric compounds are given in an earlier publication of Conflant *et al.*⁽⁴⁾. The β -phase transforms congruently to the δ -phase. δ - Bi_2O_3 has a cubic fluorite structure, which becomes rhombohedrally distorted for $X_{\text{CaO}} > 0.32$, probably because of the onset of ordering.

Burton *et al.*⁽²⁾ determined the phase diagram by X-ray

analysis of quenched samples. Levin and Roth⁽⁵⁾ used HTXRD to study δ - β equilibria in Bi_2O_3 -rich part of the system. A slightly modified version of the phase diagram has been given by Roth *et al.*⁽⁶⁾. Although their results are generally in good agreement with those of Conflant *et al.*⁽¹⁾, the stoichiometry of two compounds were revised. Following complete crystal structure determination using neutron diffraction Rietveld analysis and second harmonic generation, stoichiometry of the compound $\text{Bi}_{10}\text{Ca}_7\text{O}_{22}$ was changed to $\text{Bi}_6\text{Ca}_4\text{O}_{13}$ ⁽⁷⁾⁽⁸⁾. Similarly, measurements on single crystals reveal that the compound $\text{Bi}_6\text{Ca}_7\text{O}_{16}$ is more correctly represented as $\text{Bi}_2\text{Ca}_2\text{O}_5$ ⁽⁸⁾.

Vstavskaya *et al.*⁽³⁾ used visual observation to identify melting temperatures, and XRD on quenched samples, to map the phase diagram. The compound $\text{Bi}_{14}\text{Ca}_5\text{O}_{26}$ does not appear in their diagram. Also they find β -phase to be stable upto melting. This discrepancy may arise from a slower quenching rate employed by Vstavskaya *et al.*⁽³⁾, which was probably not sufficient to prevent $\delta \rightarrow \beta$ transformation. Studies using HTXRD are probably more reliable in establishing phase equilibria involving the solid solutions. The phase diagram shown in Fig. 1 is composed primarily from the results of Conflant *et al.*⁽¹⁾, Burton *et al.*⁽²⁾ and Roth *et al.*⁽⁶⁾. Stoichiometry of the two CaO-rich compounds are based on more recent struc-

Fig. 1 Phase diagram of the pseudo-binary system Bi_2O_3 -CaO based primarily on the results of Conflant *et al.*⁽¹⁾, Burton *et al.*⁽²⁾, and Roth *et al.*⁽⁶⁾.

ture refinements⁽⁷⁾⁽⁸⁾. Although there is no major controversy on the general topology of the diagram given in the three primary references⁽¹⁾⁽²⁾⁽⁶⁾, there are minor differ-

ences in the reported decomposition temperatures and compositions of solid solutions. Averaged values are used in Fig. 1. Table 1 summarizes crystallographic data on all phases in the Bi-Ca-O system. The rhombohedral β -phase appears in two forms. The transition from the low temperature (β_2) to the high temperature form (β_1) is accompanied by a sharp increase in oxygen ion conductivity⁽⁹⁾ and a large endothermic peak in DTA⁽¹⁾.

Baek and Virkar⁽¹⁰⁾ have reported measurements on the activity of CaO in various phase-fields of the system Bi_2O_3 -CaO in the temperature range 870 to 950 K using solid state cells based on CaF_2 as the solid electrolyte. They estimated the activity of Bi_2O_3 as a function of composition at 903 K using Gibbs-Duhem integration. Unfortunately, the compositions reported in Fig. 4 of their paper are not consistent with data reported in Table I. Also, emfs shown in Fig. 4 as a function of temperature are not fully consistent with the phase diagram.

Shimpo and Nakamura⁽¹¹⁾ measured the activity of Bi_2O_3 in the two-phase field $\text{CaO} + \text{Bi}_6\text{Ca}_7\text{O}_{16}$ using yttria-stabilized zirconia solid electrolyte in the temperature range 825 to 960 K. From this information, they derived the standard Gibbs energy of formation of $\text{Bi}_6\text{Ca}_7\text{O}_{16}$. They also measured CaO activity in various two-phase fields by equilibrating the oxide mixtures with CaCO_3 and measuring equilibrium CO_2 pressure. The partial pressure of CO_2 in the reaction tube was controlled by flowing gas mixtures of CO_2 , O_2 and N_2 . The equilibrium temperature for the dissociation of CaCO_3 correspond-

Table 1 Crystallographic data on condensed phases in the system Bi-Ca-O.

Compound	Lattice parameters						Structure	Ref.
	<i>a</i> (nm)	<i>b</i> (nm)	<i>c</i> (nm)	α	β	γ		
α - Bi_2O_3	0.5850	0.8165	0.7510		112.98°		Monoclinic $\text{P2}_1/\text{c}$	(14)
δ - Bi_2O_3 ($T=1047$ K)	0.5660						Cubic $\text{Fm}3\text{m}$	(14)
CaO	0.4811						Cubic $\text{Fm}3\text{m}$	(15)
Bi_3Ca_5	1.2723	0.9667	0.8433				Orthorhombic Pnma	(16)
$\text{Bi}_{10}\text{Ca}_{11}$	1.2222		1.7793				Tetragonal $\text{I4}/\text{mmm}$	(17)
β_2 solid solution								
$X_{\text{CaO}}=0.25$ $T=973$ K	0.3980		2.8260			120°	Rhombohedral $\text{R}\bar{3}\text{m}$	(1)
$X_{\text{CaO}}=0.23$	0.3966		2.7823			120°	Rhombohedral $\text{R}\bar{3}\text{m}$	(18)
$X_{\text{CaO}}=0.30$	0.3939		2.7856			120°	Rhombohedral $\text{R}\bar{3}\text{m}$	(18)
β_1 solid solution								
$X_{\text{CaO}}=0.25$ $T=1023$ K	0.4000		2.8540			120°	Rhombohedral $\text{R}3\text{m}$	(1)
γ solid solution								
$T=1093$ K	0.4262						Cubic	(1)
	0.4246						Cubic $\text{Im}3\text{m}$	(19)
$\text{Bi}_{14}\text{Ca}_5\text{O}_{26}$	0.9934	1.5034	1.5008	82.65°	85.27°	77.17°	Triclinic P1	(2)
Bi_2CaO_4	1.6613	1.1590	1.3994		134.05°		Monoclinic $\text{C2}/\text{c}$	(20)
	1.4002	1.1596	1.2198		101.54°		Monoclinic $\text{I2}/\text{a}$ ($\text{C2}/\text{c}$)	(21)
$\text{Bi}_6\text{Ca}_4\text{O}_{13}$	1.7365	0.5940	0.7219				Orthorhombic C2mm	(7)(8)
$\text{Bi}_2\text{Ca}_2\text{O}_5$	1.0112	1.0390	1.0475	116.86°	107.16°	92.92°	Triclinic P1	(22)

ing to each value of partial pressure of CO_2 was determined using thermogravimetry. By combining the emf and the thermogravimetric data, they deduced the free energies of formation of four ternary compounds. Unfortunately, the stoichiometry of the two CaO-rich compounds used in the interpretation of the thermodynamic data obtained by Baek and Virkar⁽¹⁰⁾ and Shimpo and Nakamura⁽¹¹⁾ are based on the phase diagram of Conflant *et al.*⁽¹⁾. Recent revisions⁽⁷⁾⁽⁸⁾ of the stoichiometry of two CaO-rich compounds necessitate reinterpretation of their data.

More recently, Idemoto *et al.*⁽¹²⁾ have measured the enthalpy of formation of two compositions $\text{Bi}_{0.46}\text{Ca}_{0.54}\text{O}_{1.23}$ ($\text{Bi}_6\text{Ca}_7\text{O}_{16}$) and $\text{Bi}_{0.59}\text{Ca}_{0.41}\text{O}_{1.30}$ ($\text{Bi}_{10}\text{Ca}_7\text{O}_{22}$) using 1.53 M HClO_4 as the solvent at 298 K. There is a large difference between the enthalpies of formation of ternary oxides obtained from the high temperature measurements of Shimpo and Nakamura⁽¹¹⁾ and room temperature calorimetry⁽¹²⁾. For example, for the compound $\text{Bi}_6\text{Ca}_7\text{O}_{16}$ emf data⁽¹¹⁾ suggests a value of -84.1 kJ/mol for enthalpy of formation from component oxides, where as calorimetric measurements give a value of -136.3 kJ/mol. For the compound $\text{Bi}_{10}\text{Ca}_7\text{O}_{22}$ measurements of Shimpo and Nakamura⁽¹¹⁾ suggest an enthalpy of formation of -62.2 kJ/mol compared to a value of -175.5 kJ/mol from calorimetry⁽¹²⁾. In view of these serious discrepancies and wrong stoichiometry for two compounds employed in earlier thermodynamic studies, a reinvestigation of the system Bi–Ca–O was undertaken.

II. Measurement Strategy: Combined Use of Oxide and Fluoride Electrolytes

The activity of CaO in various phase fields in the system Bi_2O_3 –CaO can be measured as a function of temperature using solid state cells based on CaF_2 . To obtain free energies of formation of interoxide compounds from the emf data, Gibbs-Duhem integration across the single phase field of β is necessary. Accurate measurement of the chemical potential of CaO in single phase field is rather difficult, since the electrode in such a case is monovariant. Small perturbations during measurement can cause changes in emf. Higher accuracies are obtained when chemical potentials in two-phase fields are measured, since equilibria defining potentials at the electrodes are invariant at constant temperature and pressure.

In principle, standard free energy of formation of interoxide compounds can be obtained from measurements of activity of Bi_2O_3 in two-phase fields starting from CaO side. The accuracy of such measurements decrease as one moves progressively towards compounds rich in Bi_2O_3 . For example, to obtain the free energy of formation of $\text{Bi}_{14}\text{Ca}_5\text{O}_{26}$, emf of four cells involving phase fields $\text{CaO} + \text{Bi}_2\text{Ca}_2\text{O}_5$, $\text{Bi}_2\text{Ca}_2\text{O}_5 + \text{Bi}_6\text{Ca}_4\text{O}_{13}$, $\text{Bi}_6\text{Ca}_4\text{O}_{13} + \text{Bi}_2\text{CaO}_4$, $\text{Bi}_2\text{CaO}_4 + \text{Bi}_{14}\text{Ca}_5\text{O}_{26}$ have to be combined with consequent accumulation of errors.

The inaccuracies introduced by Gibbs-Duhem integration across β -phase field and combining emf of several cells can be overcome by independent measurements of

the activity of both CaO and Bi_2O_3 in two-phase fields using solid state cells. The free energy of formation of each ternary oxide can then be obtained from activities of CaO and Bi_2O_3 in two-phase fields on either side of the compound under consideration. For the compound $\text{Bi}_{2m}\text{Ca}_n\text{O}_{3m+n}$, the standard Gibbs energy of formation from component oxides is given by:

$$\begin{aligned}\Delta G_{f,\text{ox}}^0 &= m\Delta\mu_{\text{Bi}_2\text{O}_3} + n\Delta\mu_{\text{CaO}} \\ &= RT(m \ln a_{\text{Bi}_2\text{O}_3} + n \ln a_{\text{CaO}})\end{aligned}\quad (1)$$

where values for chemical potentials and activities are those in equilibrium with the compound. Two values for the free energy of formation of each compound are obtained when activities of both components are measured in all the two-phase fields of the pseudo-binary system Bi_2O_3 –CaO, thus providing an independent check on the accuracy of measurements. For the correct design of galvanic cells, phase relations in the ternary system Bi–Ca–O should be known. Hence, a study of phase relations at 1000 K was undertaken first.

III. Experimental

1. Materials

Starting materials used for the preparation of interoxide compounds in the system Bi_2O_3 –CaO were fine powders of Bi_2O_3 and CaCO_3 , each of 99.99% purity, obtained from Johnson Matthey Chemicals Ltd. Anhydrous CaCO_3 contained in a zirconia crucible was decomposed under vacuum at 1073 K to CaO. The CaO thus formed was found to be highly reactive. Fine powders of component oxides were mixed in appropriate stoichiometric ratio, pelletized at ~ 20 MPa, contained in Pt crucible and sealed in quartz ampules under reduced pressure of $\sim 2 \times 10^4$ Pa. The ampules were heated at 1073 K for ~ 170 ks and at 1173 K for ~ 80 ks. Formation of interoxide compounds was confirmed by X-ray diffraction.

Alloys and intermetallic compounds in the system Bi–Ca were made by melting or reacting together pure metals in closed iron crucibles under flowing Ar gas. The metals were 99.9% pure. High purity Ar gas used was dehydrated by passing through anhydrous MgClO_4 and P_2O_5 , and deoxidized by passing through Cu turnings at 750 K and Ti granules at 1150 K.

Single crystal optical grade CaF_2 pellets of 5 mm thickness and 10 mm diameter were obtained from Aldrich Chemicals. Yttria-stabilized zirconia crucibles contained approximately 8 mol% Y_2O_3 . High purity O_2 gas (99.999%) was passed over CuO at 800 K to convert residual CO and H_2 to CO_2 and H_2O respectively. CO_2 was absorbed by passing the gas through NaOH. The gas was subsequently dried by passage through columns containing silica gel, anhydrous MgClO_4 and P_2O_5 .

2. Phase relations in the system Bi–Ca–O

Phase relations at 1000 K were explored by equilibrating different mixtures of alloys and compounds for

~300 ks. The large equilibration times are required in view of the low rate of formation of $\text{Bi}_{14}\text{Ca}_5\text{O}_{26}$ and Bi_2CaO_4 . The compound $\text{Bi}_6\text{Ca}_4\text{O}_{13}$ and solid solution phases δ and β form rapidly, while the γ -phase and $\text{Bi}_2\text{Ca}_2\text{O}_5$ form at intermediate rates. Preliminary experiments indicated that ~200 ks was sufficient to attain equilibrium. After equilibration, samples were quenched in liquid nitrogen. Samples containing oxides were held in closed stabilized-zirconia crucibles. The zirconia crucibles were sealed in quartz ampules under a reduced pressure of $\sim 2 \times 10^4$ Pa. Samples containing oxide mixtures were also equilibrated under pure oxygen gas at a pressure of 1.01×10^5 Pa to check for the presence of phases containing excess oxygen. Mixtures containing metallic phase were equilibrated in closed iron containers kept under pre-purified inert gas flowing at a rate of ~3 mL/s. Phase composition of quenched samples was determined using X-ray diffraction, SEM and EDAX. To check for the attainment of equilibrium, samples of the same overall composition were prepared using different starting materials. Approach to equilibrium was thus verified from different directions.

3. Emf measurements on cells based on $(\text{Y}_2\text{O}_3)\text{ZrO}_2$ as the solid electrolyte

A schematic diagram of the cell used is shown in Fig. 2. The reference electrode consisting of an equimolar mixture of Bi and Bi_2O_3 powders was contained in a stabilized-zirconia crucible with an Os wire embedded in the mixture. Mixture was tightly packed inside the crucible by ramming with a steel rod. The crucible was covered with a stabilized-zirconia lid. The contacting surfaces of the crucible and the lid were polished using diamond paste. The Os lead was taken out through a small hole in the lid. Os metal was found to be inert with liquid Bi and its oxides. The aperture was sealed with a zirconia-based cement.

The working three-phase electrode was contained in a

larger zirconia crucible. The electrode was prepared by taking Bi and two coexisting oxide phases belonging to the pseudo-binary system Bi_2O_3 -CaO in the molar ratio 1:1.5:1.5. The mixture was pelletized at 20 MPa pressure before placing in the zirconia crucible. Although Bi metal is liquid at the temperatures of measurement, liquid Bi did not segregate at the bottom of the container. Fine droplets of liquid Bi in the pellet were held by surface tension forces between surrounding oxide grains. The smaller zirconia crucible containing the reference electrode was pressed down against three-phase electrode pellet by a system of alumina tubes, slabs, and springs. The annular space between the two zirconia crucibles was packed with the three-phase mixture, composition of which was identical to that of the measuring electrode. The outer solid electrolyte crucible was also closed with a lid containing a circular hole in the centre and an aperture for Os wire contacting the working electrode. The Os wires were connected to Pt leads outside each crucible. Since both Os/Pt junctions were at the same temperature, there was no thermoelectric contribution to the cell emf. The cell assembly shown in Fig. 2 was placed inside a vertical alumina tube and suspended in the even-temperature zone (± 1 K) of a resistance furnace. A stainless steel sheet was wrapped around the alumina tube and earthed to minimize induced emf on cell leads. The top and bottom ends of the vertical alumina tube enclosing the cell were closed with brass caps. The brass caps were provided with a gas inlet and outlet and insulated provisions for electric leads. The alumina tube was flushed with pre-purified Ar gas at a flow rate of ~3 mL/s. The emf developed between the Pt leads was measured using a high impedance voltmeter. Temperature of the cell was measured by a Pt/Pt-13%Rh thermocouple placed adjacent to the zirconia crucible. The temperature was controlled to ± 1 K.

Emf of the following cells were measured as a function of temperature:

Pt, Os, $\text{CaO} + \text{Bi}_2\text{Ca}_2\text{O}_5$ + Bi $(\text{Y}_2\text{O}_3)\text{ZrO}_2$ Bi + Bi_2O_3 , Os, Pt	I
Pt, Os, $\text{Bi}_2\text{Ca}_2\text{O}_5 + \text{Bi}_6\text{Ca}_4\text{O}_{13}$ + Bi $(\text{Y}_2\text{O}_3)\text{ZrO}_2$ Bi + Bi_2O_3 , Os, Pt	II
Pt, Os, $\text{Bi}_6\text{Ca}_4\text{O}_{13} + \text{Bi}_2\text{CaO}_4$ + Bi $(\text{Y}_2\text{O}_3)\text{ZrO}_2$ Bi + Bi_2O_3 , Os, Pt	III
Pt, Os, $\text{Bi}_2\text{CaO}_4 + \text{Bi}_{14}\text{Ca}_5\text{O}_{26}$ + Bi $(\text{Y}_2\text{O}_3)\text{ZrO}_2$ Bi + Bi_2O_3 , Os, Pt	IV
Pt, Os, $\text{Bi}_{14}\text{Ca}_5\text{O}_{26} + \beta$ -phase + Bi $(\text{Y}_2\text{O}_3)\text{ZrO}_2$ Bi + Bi_2O_3 , Os, Pt	V

The reversibility of emfs were checked by microcoulometric titration in both directions. Emf was found to return to the steady value after each titration. Emf was independent of the flow rate of Ar gas (2 to 5 mL/s) around the cell and reproducible on temperature cycling. After each emf run electrodes were examined by X-ray diffraction. No significant changes in the composition of the electrodes were noted.

Fig. 2 Schematic diagram of the apparatus used for emf measurements on solid state cells based on $(\text{Y}_2\text{O}_3)\text{ZrO}_2$ as the solid electrolyte.

4. Emf measurements on cells based on CaF_2 as the solid electrolyte

Since CaF_2 is a fluoride ion conductor, emf of a cell incorporating CaF_2 as the electrolyte is determined by difference in chemical potential of fluorine at the two electrodes. The fluorine potential at each electrode is established by the reaction:

where CaO is present at unit activity in the reference electrode and at reduced activity in the working electrodes. The emf of the cell can be directly related to chemical potential of CaO at the working electrodes;

$$-2FE = \Delta\mu_{\text{CaO}} \quad (3)$$

Schematic diagram of the cell assembly incorporating CaF_2 as the electrolyte is shown in Fig. 3. The electrode pellets were spring-loaded on either side of a transparent single crystal CaF_2 with a thin Pt gauze placed between the electrode and the solid electrolyte. Pt wires, spot-welded to the Pt gauze, provided electrical leads to a high impedance voltmeter ($10^{13} \Omega$). The pellets were held together under pressure through a system consisting of springs, an alumina rod, and a flat-bottomed alumina tube with a section cut away parallel to the axis as shown in the figure. Direct contacts of the electrode pellets with an alumina rod or tube was prevented by inserting Pt foils between them. The cell was maintained under dry flowing O_2 at a pressure of 10^5 Pa . In preliminary experiments, transparent CaF_2 crystals were found to become translucent during the run. Fine opaque precipitates appeared on the outer surface of CaF_2 crystals. These precipitates were identified by selected area electron diffraction as $\text{CaO}^{(13)}$. They apparently formed by the

reaction of the crystal with residual moisture in the gas:

CaO precipitation was minimized by degassing the alumina tubes and rods under vacuum and by using improved drying procedures for O_2 gas. It can be shown from thermodynamic considerations that CaF_2 will not react with dry O_2 to form CaO .

The emf of the following cells were measured as a function of temperature:

Pt, O_2 , CaO CaF_2 $\text{CaO} + \text{Bi}_2\text{Ca}_2\text{O}_5$, O_2 , Pt	VI
Pt, O_2 , CaO CaF_2 $\text{Bi}_2\text{Ca}_2\text{O}_5 + \text{Bi}_6\text{Ca}_4\text{O}_{13}$, O_2 , Pt	VII
Pt, O_2 , CaO CaF_2 $\text{Bi}_6\text{Ca}_4\text{O}_{13} + \text{Bi}_2\text{CaO}_4$, O_2 , Pt	VIII
Pt, O_2 , CaO CaF_2 $\text{Bi}_2\text{CaO}_4 + \text{Bi}_{14}\text{Ca}_5\text{O}_{26}$, O_2 , Pt	IX
Pt, O_2 , CaO CaF_2 $\text{Bi}_{14}\text{Ca}_5\text{O}_{26} + \beta\text{-phase}$, O_2 , Pt	X
Pt, O_2 , CaO CaF_2 $\beta\text{-phase} + \alpha\text{-Bi}_2\text{O}_3$, O_2 , Pt	XI

Since CaO , CaF_2 , and O_2 gas must be in contact to fix the fluorine potential, CaF_2 was added to CaO in the preparation of the reference electrode pellet. Similarly, CaF_2 was also added to the measuring electrode pellet. Pellets were prepared by mixing components in equimolar ratio, compacting at 20 MPa and sintering in pre-purified O_2 gas at 1200 K.

Although emf of cell VI could be measured from 880 K to 1200 K, the range of temperature for successful functioning decreased gradually for subsequent cells. For cell XI, reproducible emf was obtained only at 900 K. The time required to obtain steady emf varied from approximately 70 ks at 880 K to 7 ks at 1200 K. Reversibility of the cells was checked using microcoulometry, temperature cycling and variation in gas flow rate.

IV. Results and Discussion

1. Phase relations

Isothermal section of the phase diagram of the system Bi–Ca–O at 1000 K composed from results of this study is shown in Fig. 4. The bulk compositions of the samples analyzed are shown by cross marks. Twenty-three compositions in the ternary and three compositions along the binaries were analyzed. All the solid solutions and intermetallic compounds along the binary Bi–Ca were found to be in equilibrium with pure CaO . Compositions of all the ternary phases were found to lie on the join Bi_2O_3 – CaO . The compositions of all the compounds and solid solutions were confirmed by EDAX. The information obtained from XRD was consistent with data in Table 1. All the ternary oxides are in equilibrium with Bi. Thus it is possible to equilibrate coexisting phases along the pseudo-binary Bi_2O_3 – CaO with metallic Bi to fix oxygen potential, which can be measured accurately using an oxide electrolyte. The interoxide compounds are in equilibrium with pure O_2 gas. The Bi-ion was found to be in trivalent state in all the interoxide compounds.

2. Chemical potential of Bi_2O_3 in two-phase fields

The reversible emf of cells I to V is plotted as a func-

Fig. 3 Schematic diagram of the apparatus used for emf measurement on solid state cells based on CaF_2 as the electrolyte.

Fig. 4 Isothermal section of the phase diagram of the system Bi-Ca-O at 1000 K composed from the results of this study. The average composition of the samples analyzed is shown by X.

Fig. 5 Emf of cells I to V as a function of temperature.

tion of temperature in Fig. 5. The emfs of cells I to IV exhibit a change of slope at $1001(\pm 1)$ K. This is related to $\alpha \rightarrow \delta$ transformation of Bi_2O_3 in the reference electrode. The average value of the enthalpy of transformation deduced from the change in slope of emf is $30.6(\pm 0.3)$ kJ/mol at 1001 K. Within experimental uncertainty limits, emf of cells I to IV can be expressed as a linear function of temperature. Expressions for the emf obtained by least squares regression analysis are summarized in Table 2. Uncertainty estimates corresponds to twice the standard deviation. The activity or chemical potential of Bi_2O_3 in various two-phase fields in the pseudo-binary system can be deduced from emf of cells I to

Table 2 Emf of cells based on $(\text{Y}_2\text{O}_3)_2\text{ZrO}_2$.

Cell	E (mV)	Temperature (K)
I	$74.9 - 9.17 \times 10^{-3} T (\pm 1.5)$	830–1002
	$127.7 - 6.19 \times 10^{-2} T (\pm 0.7)$	1002–1090
II	$37.9 + 7.13 \times 10^{-3} T (\pm 1.4)$	830–1001
	$90.4 - 4.54 \times 10^{-2} T (\pm 0.6)$	1001–1090
III	$31.0 - 2.78 \times 10^{-3} T (\pm 1)$	830–1000
	$84.4 - 5.61 \times 10^{-2} T (\pm 0.4)$	1000–1050
IV	$19.6 + 1.07 \times 10^{-3} T (\pm 1)$	830–1002
	$72.4 - 5.16 \times 10^{-2} T (\pm 0.4)$	1002–1050
V	$11.6 (\pm 0.6)$	900

Table 3 Chemical potential of Bi_2O_3 in two-phase fields of the system Bi_2O_3 -CaO.

Phase field	$\Delta\mu_{\text{Bi}_2\text{O}_3}$, J/mol
$\text{CaO} + \text{Bi}_2\text{Ca}_2\text{O}_5$	$-43360 + 5.31 T (\pm 900)$
$\text{Bi}_2\text{Ca}_2\text{O}_5 + \text{Bi}_6\text{Ca}_4\text{O}_{13}$	$-21940 - 4.13 T (\pm 800)$
$\text{Bi}_6\text{Ca}_4\text{O}_{13} + \text{Bi}_2\text{CaO}_4$	$-17950 + 1.61 T (\pm 600)$
$\text{Bi}_2\text{CaO}_4 + \text{Bi}_{14}\text{Ca}_5\text{O}_{26}$	$-11350 - 0.62 T (\pm 600)$
$\text{Bi}_{14}\text{Ca}_5\text{O}_{26} + \beta$	$-6720 (\pm 300)$ at 900 K

V. The emf is directly related to the chemical potential of Bi_2O_3 by the relation,

$$-6FE = \Delta\mu_{\text{Bi}_2\text{O}_3} = RT \ln a_{\text{Bi}_2\text{O}_3} \quad (5)$$

The derived chemical potentials are given in Table 3.

3. Chemical potential of CaO in two-phase fields

The variation of emf of cells VI to XI with temperature is displayed in Fig. 6. Emf of cell VI is almost zero, independent of temperature. Emf of cells VII, VIII and IX vary linearly with temperature, whereas emf of cell X exhibits nonlinear variation, probably due to change in composition of β -phase with temperature. Emf of cell XI could be obtained only at 900 K. Emf of cells IX and X appear to converge at $1026(\pm 4)$ K indicating decomposition of $\text{Bi}_{14}\text{Ca}_5\text{O}_{26}$ to β -phase and Bi_2CaO_4 . Expressions for emf of cells VI to IX obtained by least square regression analysis are given in Table 4. Equations for the chemical potential of CaO deduced from emf are presented in Table 5.

4. Gibbs energies of formation of the interoxide compounds and solid solutions

The standard Gibbs energy of formation of each ternary oxide can be computed from the chemical potentials of Bi_2O_3 and CaO in phase fields involving the compound. Thus two values for the free energy of formation can be derived from chemical potentials of component binary oxides on either side of the ternary compound using eq. (1). The two values for the Gibbs energy thus derived for each compound are found to be in close agreement indicating good internal consistency. The mean values for the integral free energy of formation of the interoxide compounds and solid solutions are given in Table 6. The maximum difference in the value of $\Delta G_f^0(\text{Bi}_{2m}\text{Ca}_n\text{O}_{3m+n})/(m+n)$ is 170 J/mol of the component binary oxides.

Fig. 6 Emf of cells VI to XI as a function of temperature.

Table 4 Emf of cells based on CaF_2 .

Cell	E (mV)	Temperature (K)
VI	$0(\pm 1)$	880–1200
VII	$57.8 - 2.69 \times 10^{-2}T (\pm 1)$	880–1120
VIII	$69.9 - 1.09 \times 10^{-3}T (\pm 1)$	880–1050
IX	$108.9 - 1.77 \times 10^{-2}T (\pm 1)$	880–1010
X	$101.5(\pm 2)$	1000
	$131(\pm 2)$	900
XI	$233(\pm 4)$	900

Table 5 Chemical potential of CaO in two-phase fields of the system Bi_2O_3 –CaO.

Phase field	$\Delta\mu_{\text{CaO}}$, J/mol
CaO + $\text{Bi}_2\text{Ca}_2\text{O}_5$	$0(\pm 200)$
$\text{Bi}_2\text{Ca}_2\text{O}_5$ + $\text{Bi}_6\text{Ca}_4\text{O}_{13}$	$-11150 + 5.20T (\pm 200)$
$\text{Bi}_6\text{Ca}_4\text{O}_{13}$ + Bi_2CaO_4	$-13490 + 0.21T (\pm 200)$
Bi_2CaO_4 + $\text{Bi}_{14}\text{Ca}_5\text{O}_{26}$	$-21020 + 3.42T (\pm 200)$
$\text{Bi}_{14}\text{Ca}_5\text{O}_{26}$ + β -phase	$-19590(\pm 400)$ at 1000 K $-25280(\pm 400)$ at 900 K
β -phase + α - Bi_2O_3	$-44970(\pm 800)$ at 900 K

Table 6 Integral molar free energies of formation of interoxide compounds and solid solutions.

Formation reaction	ΔG_f° , J/mol
$\alpha\text{-Bi}_2\text{O}_3 + 2\text{CaO} \rightarrow \text{Bi}_2\text{Ca}_2\text{O}_5$	$-43800 + 5.79T (\pm 900)$
$3\alpha\text{-Bi}_2\text{O}_3 + 4\text{CaO} \rightarrow \text{Bi}_6\text{Ca}_4\text{O}_{13}$	$-109800 + 7.04T (\pm 2300)$
$\alpha\text{-Bi}_2\text{O}_3 + \text{CaO} \rightarrow \text{Bi}_2\text{CaO}_4$	$-31910 + 2.31T (\pm 650)$
$7\alpha\text{-Bi}_2\text{O}_3 + 5\text{CaO} \rightarrow \text{Bi}_{14}\text{Ca}_5\text{O}_{26}$	$-184560 + 12.76T (\pm 4320)$
$0.7\alpha\text{-Bi}_2\text{O}_3 + 0.3\text{CaO} \rightarrow \text{Bi}_{1.4}\text{Ca}_{0.3}\text{O}_{2.4}(\beta)$	$-12290(\pm 300)$ at 900 K
$0.78\alpha\text{-Bi}_2\text{O}_3 + 0.22\text{CaO} \rightarrow \text{Bi}_{1.56}\text{Ca}_{0.22}\text{O}_{2.56}(\beta)$	$-9890(\pm 180)$ at 900 K

The standard free energy of formation of $\text{Bi}_2\text{Ca}_2\text{O}_5$ obtained in this study is compared with results derived from the measurements of Baek and Virkar⁽¹⁰⁾ and Shimp and Nakamura⁽¹¹⁾ in Fig. 7. It is to be noted that both earlier groups of investigators designated the $\text{Bi}_2\text{Ca}_2\text{O}_5$ as $\text{Bi}_6\text{Ca}_7\text{O}_{16}$. Values for $\text{Bi}_2\text{Ca}_2\text{O}_5$ recalculated using the measurements reported in the earlier publications⁽¹⁰⁾⁽¹¹⁾ are displayed in the Fig. 7. Although Baek and Virkar⁽¹⁰⁾ have measured emf as a function of temperature, there is incompatibility between data reported in Fig. 4 and Table I of their paper⁽¹⁰⁾. From the emf measurements, activity of CaO can be obtained directly. To deduce activity of Bi_2O_3 Gibbs-Duhem equation has to be integrated across the β -phase field. The authors⁽¹⁰⁾ have performed the integration only at 903 K. Hence, the standard free energy of formation of $\text{Bi}_2\text{Ca}_2\text{O}_5$ has been calculated only at 903 K based on results given in Table II of Baek and Virkar⁽¹⁰⁾. The uncertainty in their data is evaluated based on reproducibility of their emfs, ranging from ± 1 mV for Bi_2O_3 -rich compositions to ± 5 mV for CaO-rich phases. The results obtained in this study are more nega-

Fig. 7 Comparison of the standard free energy of formation of $\text{Bi}_2\text{Ca}_2\text{O}_5$ obtained in this study with data derived of Baek and Virkar⁽¹⁰⁾ and Shimp and Nakamura⁽¹¹⁾.

tive by ~ 3 kJ/mol than those obtained from the earlier investigations⁽¹⁰⁾⁽¹¹⁾. Faulty designs and procedures in potentiometric measurements generally result in smaller values of emf and derived free energies. Baek and Virkar⁽¹⁰⁾ have reported small drift in the emf of their cells at high temperature.

The second law enthalpy of formation of $\text{Bi}_2\text{Ca}_2\text{O}_5$ from component oxides at an average temperature of 1025 K obtained from the results of this study is $-43.8(\pm 2.7)$ kJ/mol. This compares favourably with the calorimetric value of -136.3 kJ/mol for $\text{Bi}_6\text{Ca}_7\text{O}_{16}$ reported by Idemoto *et al.*⁽¹²⁾ at 298 K. The calorimetric value reinterpreted in terms of $\text{Bi}_2\text{Ca}_2\text{O}_5$ approximates to -45.5 kJ/mol. Although an uncertainty estimate has not been provided by Idemoto *et al.*⁽¹²⁾, the error limit is probably ± 3 kJ/mol. Heat capacity data for $\text{Bi}_2\text{Ca}_2\text{O}_5$ are not available to assess the effect of temperature on the enthalpy of formation. The corresponding values from the high temperature free energy measurements of Shimpo and Nakamura⁽¹¹⁾ are -184.1 kJ/mol of $\text{Bi}_6\text{Ca}_7\text{O}_{16}$ or -28.0 kJ/mol of $\text{Bi}_2\text{Ca}_2\text{O}_5$. Clearly, the temperature coefficient of emf reported by Shimpo and Nakamura⁽¹¹⁾ is compatible neither with the results of this study nor with calorimetry. This points to the temperature-dependent systematic errors in the data reported by Shimpo and Nakamura⁽¹¹⁾. Probably true equilibrium was not attained in their measurement at low temperature. As temperature is increased, their results move in the direction of data obtained in this study. Results of this study are in good agreement with calorimetric data and fair agreement with absolute values of free energy reported earlier⁽¹⁰⁾⁽¹¹⁾.

The standard free energy of formation of $\text{Bi}_6\text{Ca}_4\text{O}_{13}$ obtained in this study is compared with the values recalculated from the data of Baek and Virkar⁽¹⁰⁾ and Shimpo and Nakamura⁽¹¹⁾ in Fig. 8. It is to be noted that the two earlier investigators⁽¹⁰⁾⁽¹¹⁾ labelled the compound $\text{Bi}_6\text{Ca}_4\text{O}_{13}$ as $\text{Bi}_{10}\text{Ca}_7\text{O}_{22}$. The free energy of formation obtained in this study is more negative by $\sim 8\%$. The second law enthalpy of formation of $\text{Bi}_6\text{Ca}_4\text{O}_{13}$ at a mean temperature of 990 K obtained from the results of this study is $-109.8(\pm 6.9)$ kJ/mol. This can be compared with a value of -175.5 kJ/mol of $\text{Bi}_{10}\text{Ca}_7\text{O}_{22}$ or ~ -105 kJ/mol of $\text{Bi}_6\text{Ca}_4\text{O}_{13}$ obtained from Idemoto *et al.*⁽¹²⁾ at 298 K. The uncertainty in calorimetric measurement is estimated as ± 8 kJ/mol of $\text{Bi}_6\text{Ca}_4\text{O}_{13}$. The enthalpy of formation obtained from the free energy measurements of Shimpo and Nakamura⁽¹¹⁾ is -62.2 kJ/mol of $\text{Bi}_{10}\text{Ca}_7\text{O}_{22}$ or -37.32 kJ/mol of $\text{Bi}_6\text{Ca}_4\text{O}_{13}$. The results of this study agree with the calorimetric data within uncertainty limits. Present results are also in fair agreement with the earlier free energy measurements. Again, the temperature coefficient of free energy reported by Shimpo and Nakamura⁽¹¹⁾ is not compatible with the result of this study and the calorimetric data of Idemoto *et al.*⁽¹²⁾

The standard Gibbs energy of formation of compound Bi_2CaO_4 from component oxides obtained in this study is compared with data reported by Shimpo and

Fig. 8 Comparison of the standard free energy of formation of $\text{Bi}_6\text{Ca}_4\text{O}_{13}$ obtained in this study with data derived of Baek and Virkar⁽¹⁰⁾ and Shimpo and Nakamura⁽¹¹⁾.

Fig. 9 Comparison of the standard free energy of formation of Bi_2CaO_4 obtained in this study with data derived of Baek and Virkar⁽¹⁰⁾ and Shimpo and Nakamura⁽¹¹⁾.

Nakamura⁽¹¹⁾ and Baek and Virkar⁽¹⁰⁾ in Fig. 9. If the measurements of Shimpo and Nakamura⁽¹¹⁾ are reassessed in terms of stoichiometry of compounds shown in Fig. 1, their values become more negative by ~ 2.7 kJ/mol. The results obtained in this study are more negative by ~ 3.3 kJ/mol than the values recalculated from the measurements of Shimpo and Nakamura⁽¹¹⁾, and ~ 2 kJ/mol

Fig. 10 Comparison of the standard free energy of formation of $\text{Bi}_{14}\text{Ca}_5\text{O}_{26}$ obtained in this study with data derived of Baek and Virkar⁽¹⁰⁾ and Shimpo and Nakamura⁽¹¹⁾.

more negative than the values obtained from Baek and Virkar⁽¹⁰⁾. Calorimetric measurements have not been performed on the compound Bi_2CaO_4 .

For the compound $\text{Bi}_{14}\text{Ca}_5\text{O}_{26}$, Fig. 10 compares the free energy of formation obtained in this study with the data of Shimpo and Nakamura⁽¹¹⁾ and Baek and Virkar⁽¹⁰⁾. The free energy of formation reassessed from the measurements of Shimpo and Nakamura⁽¹¹⁾ based on the more recent information on the stoichiometry of interoxide compounds is ~ 20 kJ/mol more negative than values reported in their paper. Data obtained in this study is $\sim 12\%$ more negative than revised values obtained from Shimpo and Nakamura⁽¹¹⁾ and Baek and Virkar⁽¹⁰⁾. The free energies of formation of β -phase for two phase boundary compositions obtained at 900 K are tabulated in Table 6.

The free energy of mixing for the system Bi_2O_3 –CaO at 900 K is displayed in Fig. 11. The free energy of mixing value for the compound $\text{Bi}_{2m}\text{Ca}_n\text{O}_{3m+n}$ is obtained by dividing the standard Gibbs energy of formation from component oxides by $(m+n)$. The free energy of mixing curve is compatible with the phase diagram displayed as Fig. 1. The difference in the free energy of formation of interoxide compounds obtained in this study and those reported by Shimpo and Nakamura⁽¹¹⁾ arise primarily from difference in values for the compound $\text{Bi}_2\text{Ca}_2\text{O}_5$. The chemical potentials of CaO in two-phase fields obtained in this study using cells based on CaF_2 are in reasonable agreement (± 1.8 kJ/mol) with data obtained by Shimpo and Nakamura⁽¹¹⁾ from dissociation pressure

Fig. 11 The free energy of mixing for system Bi_2O_3 –CaO at 900 K.

Fig. 12 Comparison of the chemical potential of CaO in two-phase fields obtained in this study with those of Shimpo and Nakamura⁽¹¹⁾.

measurements, as shown in Fig. 12. The various two-phase fields are labelled according to compound designations given in Fig. 1. The relatively large error bar associated with values for chemical potential of CaO obtained from Shimpo and Nakamura⁽¹¹⁾ is caused by uncertainty (± 2 kJ/mol) in the free energy of formation of CaCO_3 .

V. Conclusions

A study of the isothermal section of the phase diagram

for the system Bi–Ca–O at 1000 K indicate four interoxide compounds ($\text{Bi}_2\text{Ca}_2\text{O}_5$, $\text{Bi}_6\text{Ca}_4\text{O}_{13}$, Bi_2CaO_4 , $\text{Bi}_{14}\text{Ca}_5\text{O}_{26}$) and two solid solution phases (δ and β) along the pseudo-binary join Bi_2O_3 –CaO. In all the compounds, Bi-ion was found to be in trivalent state. All the oxide phases were found to be in equilibrium with pure liquid Bi. Alloys and intermetallic compounds coexist with CaO.

Gibbs energies of formation of ternary oxides from their component binaries were determined accurately by combined deployment of two different solid electrolytes. Activity of CaO in two-phase fields of the pseudo-binary system Bi_2O_3 –CaO were measured using cells incorporating single crystal CaF_2 . Activity of Bi_2O_3 in two-phase fields were measured with cells based on yttria-stabilized zirconia. The combined use of two types of solid state cells enabled two independent assessments of free energy of formation of each interoxide compound. The internal consistency of the results was thus verified. The free energies of formation of interoxide compounds are summarized in Table 6. On the average, free energy values obtained in this study at high temperature are $\sim 10\%$ more negative than those reported earlier by Baek and Virkar⁽¹⁰⁾ and Shimpo and Nakamura⁽¹¹⁾. The “second law” enthalpy of formation of $\text{Bi}_2\text{Ca}_2\text{O}_5$ and $\text{Bi}_6\text{Ca}_4\text{O}_{13}$ obtained in this study agree with calorimetric measurements of Idemoto *et al.*⁽¹²⁾ within uncertainty limits. It is shown that the temperature coefficients of free energy reported by Shimpo and Nakamura⁽¹¹⁾ are not compatible with calorimetric information⁽¹²⁾.

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