ABSTRACT

The determination of precise and accurate thermodynamic data on ternary oxides together with a clear understanding of the phase relations in multicomponent oxide systems is essential for the processing of materials with tailor made properties for specific technological applications. In addition, such data are indispensable for the development of newer materials besides evaluating their high temperature compatibilities with their substrate materials as well as their service environment. There are various experimental techniques available for the determination of the thermodynamic data on oxide materials such as those based on vapour pressure, gas equilibrium, thermogravimetry, solid electrolyte galvanic cell (SEGC) and calorimetry. Among these, the SEGC technique still appears to be the most attractive one in view of its high precision and reliability on account of the true equilibrium nature of the emf measurements. Solid electrolytes based on stabilized zirconia (SZ) and doped thoria (DT) were used extensively during the last four decades for the thermodynamic characterization of oxides in the SEGC technique. There are certain inherent limitations of these solid electrolytes particularly with respect to their operation under highly reducing oxygen partial pressure conditions and at temperatures lower than 700 K. These restrictions preclude the use of SZ and DT based electrolytes for evaluating the thermodynamic stabilities of very stable oxides such as LiNbO₃ and LiTaO₃, which are employed as wave guides in electro-optic devices. In this context, a search of the available literature on the
development of new electrolytes was made and the first chapter gives a review on the quest for new solid electrolytes.

The second chapter gives a description of the experimental techniques used for the synthesis and characterization of the oxide materials reported in this thesis.

Chapter 3 describes the development and characterization of a novel composite electrolyte along with some investigations on dilute electrolytes. On the basis of the information gathered from the literature, a composite electrolyte made up of a mixture of α-alumina and sodium-beta-alumina (ASBA) was developed and its performance for measuring lower oxygen partial pressures (characteristic of highly stable oxides) was evaluated. This was done using binary metal/metal oxide (M/MO) buffer mixtures and $\Delta G^\circ_r (Ta_2O_5)$ as well as $\Delta G^\circ_r (Al_2O_3)$ were determined using ASBA in conjunction with suitable reference electrodes. It was verified that ASBA is a promising electrolyte for monitoring oxygen partial pressures below the electrolytic domain boundary of even DT based electrolytes. As a part of the electrical characterization of ASBA, thermoelectric power (TEP) measurements were carried out and the average TEP for the composite over the temperature range 620-1250 K was determined to be 430 $\mu$V/K. Without resorting to the much complicated AC impedance measurements, the activation energy for electrical conduction of Na$^+$ in ASBA was determined from TEP measurements to be 17.5 kJ.mol$^{-1}$. In addition, CaF$_2$ when used in the dilute electrolyte mode was shown to behave reversibly with
respect to $O^{2-}$ ions and hence could be employed for oxygen potential measurements. Similar experiments conducted on 8 mole % yttria stabilized zirconia demonstrated its applicability for direct fluorine potential measurements.

Chapter 4 describes the applications of ASBA for the thermodynamic characterization of $Li_3NbO_4$ and $LiTa_3O_8$ which are also candidate electro-optic device materials. The data so accrued from these measurements were used to construct a partial phase diagram of the Li-Nb-O as well as the Li-Ta-O system.

The thermodynamic data obtained on the only two ternary oxides in Sm-Cu-O system namely $Sm_2CuO_4$ and $SmCuO_2$ using 15 mole % calcia stabilized zirconia as the solid electrolyte are summarized in chapter 5. These data were also corroborated by a set of controlled atmosphere non-isothermal TG experiments on $Sm_2CuO_4$ while those on $SmCuO_2$ by quenching studies followed by X-ray diffraction analyses. A partial phase diagram on Sm-Cu-O system was constructed and its consistency with the thermodynamic data so accrued on the ternary oxides was duly established.

The subsystems of the quaternary rare-earth (RE)-Ba-Cu-O system are of relevance in the assessment of the thermodynamic stabilities of the ceramic superconductors of the type $REBa_2Cu_3O_{7-x}$. A survey of literature revealed that the RE-Ba-O system was the least investigated compared to the others namely RE-Cu-O and Ba-Cu-O. Hence the thermodynamic characterization of ternary oxides of the type $Ln_2BaO_4$ ($Ln = Nd, Sm, Eu$ or Gd) in the Ln-Ba-O system were
carried out using the CaF$_2$-based emf technique under an environment of unit oxygen fugacity and the results obtained are presented in Chapter 6.

Chapter 7 describes the thermodynamic characterization of the perovskite type RECoO$_3$ (RE = Nd, Sm, Eu, Gd or Dy) compounds using the oxide SEGCE technique and the Gibbs energy data so determined were compared with reference to the distortion from the stable perovskite structure in order to identify systematic trend if any in their stabilities at higher temperatures.

Thus, the original work reported in this thesis is expected to contribute significantly to the understanding of the high temperature stabilities of some of the ternary oxides which are of relevance to materials science.