This thesis reports the original results on the novel applications of the emf method based on CaF$_2$ solid electrolyte in the thermodynamic characterization of multicomponent alloys namely, the austenitic stainless steels, compounds of fission product-chemical interaction, namely, those in Cr-Te system, and that of ternary oxides, namely, $Y_2\text{BaO}_4$ and $Y_2\text{Cu}_2\text{O}_5$ which are the phases coexisting with the 'green' phase, $Y_2\text{BaCuO}_5$ in the pseudo-ternary $Y_2\text{O}_3$-$\text{BaO}$-$\text{CuO}$ phase diagram containing the recently discovered ceramic superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ as one of the phases.

The solid electrolyte electromotive force method had paved the way for a precise and accurate determination of the thermodynamic properties of compounds and alloys during the past 30 years. The exemplary precision of the method is due to the capability of measuring the open circuit voltage of galvanic cells within a very narrow scatter of the order of one millivolt. Of the many solid electrolytes available, single crystal CaF$_2$ has not been as extensively employed in the galvanic cells for the thermodynamic property measurements of compounds and alloys as those based on stabilized zirconia. The merits, limitations and the factors affecting these fluorine concentration cells are therefore discussed to highlight the scope of the method.

One of the limitations of the CaF$_2$-emf method has been the lack of availability of precise Gibbs energy data on binary metal fluorides which could serve as the reference electrode materials. This lacuna is at least partly due to the rather narrow temperature range of operation of Daniel type fluoride cells as a consequence of pronounced volatility and increased reactivity of fluorides.
at high temperatures. The temperature range of such cells was extended by using beta-alumina as an electrolyte, and the equivalence of the emf output of the galvanic cells comprising of Fe/FeF$_2$ or Cr/CrF$_2$ against Ni/NiF$_2$ (using CaF$_2$ as electrolyte) on one hand and Fe/FeF$_2$/NaF or Cr/CrF$_2$/NaF against Ni/NiF$_2$/NaF (using beta-alumina as electrolyte) on the other, was demonstrated. Using these emf results, expressions for the standard Gibbs energy of formation, $\Delta G_f^\circ$ of FeF$_2$(s) and CrF$_2$(s) were derived over the range 500 to 1065 K for use as reference data in galvanic cell applications.

A novel metastable emf method using CaF$_2$ was developed for the direct determination of thermodynamic activity of both the components of a binary alloy. The feasibility of this method was demonstrated in the case of a well-characterized Ni-25a/o Cr alloy by comparing the experimental results on $a_Cr$ and $a_Ni$ with those reported in the literature ($a_Cr$ from experiments and $a_Ni$ derived from Gibbs-Duhem integration).

This novel metastable emf method was applied for the measurement of activities of major metallic constituents, viz., Fe, Cr, Ni and Mn (and Mo wherever applicable) in the austenitic phase separated from the stainless steels of the type AISI 304, 316 and 316LN which are used as structural alloys in Fast Breeder Nuclear Reactors. The application of these activity data in:

(a) deriving the standard Gibbs energy of formation ($\Delta G_f^\circ$) of the complex chromium-rich carbide of the formula $M_{23}C_6$,

(b) comparing the sensitization behaviour of 304 and 316 stainless steels,

(c) computing the threshold oxygen levels in liquid Na(l)/stainless steel system for the formation of corrosion products, and

(d) constructing revised Ellingham diagrams for binary oxide and fluoride scale formation,
are also discussed.

As tellurium is one of the most deleterious fission products in FBRs, it is necessary to determine the stability of Cr-Te alloys for an understanding of fission product-clad chemical interactions. Since such data are scarce in the literature, CaF$_2$-emf method was employed to derive the $\Delta G_f^\circ$ of Cr$_7$Te$_8$, Cr$_5$Te$_6$ and Cr$_3$Te$_4$ phases in Cr-Te system in the temperature range useful to fast breeder reactors.

Yet another interesting application of CaF$_2$ as electrolyte in galvanic cells is the feasibility of determining the $\Delta G_f^\circ$ of ternary oxides under one atmosphere oxygen pressure. This method is particularly promising in the thermodynamic characterization of the high temperature ceramic superconductor YBa$_2$Cu$_3$O$_{7-x}$ (1-2-3 compound) which is stable only under an oxygen pressure of nearly one atmosphere at high temperatures. To facilitate the determination of $\Delta G_f^\circ$ of 1-2-3 compound, those on the constituent ternary compounds such as Y$_2$BaO$_4$ and Y$_2$Cu$_2$O$_5$ are required. These data were generated by monitoring the BaO potential in Y$_2$BaO$_4$/Y$_2$O$_3$/BaF$_2$ measured against BaZrO$_3$/ZrO$_2$/BaF$_2$ and Y$_2$O$_3$ potential in Y$_2$Cu$_2$O$_5$/CuO/YF$_3$ against Y$_2$O$_3$/YF$_3$ using CaF$_2$ as electrolyte under one atmosphere of oxygen.

The prospects of similar applications of CaF$_2$-emf method to other alloys and compounds are also discussed in this thesis.