Conclusions
The study of bismuth based electrolyte, in the present thesis, was undertaken to establish its potential applications in solid oxide fuel cells. The performance of a solid oxide fuel cell depends primarily on ionic conductivity of its electrolyte so there has been a continuous effort to develop electrolytes with higher ionic conductivity at intermediate temperatures. Though Yttria stabilized zirconia has been used as a base electrolyte in solid oxide fuel cell. However, below 1000°C, its ionic conductivity decreases drastically. Therefore, new electrolytes which have good ionic conductivity in the temperature range of 500-800°C are required to make cost effective SOFC. Based on this, the thesis work was carried out on doped bismuth vanadate (BIMEVOX) based solid electrolytes.

In the present work four new oxide-ion conductors belonging to BIMEVOX family, which can be formulated as Bi$_4$Me$_x$V$_{2-x}$O$_{11-[(5-n)x/2]\cdot \delta}$, where Me = Ca$^{2+}$, Ba$^{2+}$, Sn$^{4+}$ and Mn$^{4+}$ cations, were prepared by conventional solid state reactions. The composition dependence of polymorphism of these systems was studied by various
techniques like FT-IR spectroscopy, X-ray powder diffraction technique and differential thermal analysis (DTA), whereas the ionic-conductivity was calculated by AC impedance spectroscopy.

It has been found that for Ca\(^{2+}\) and Ba\(^{2+}\) substituted system α-phase is stabilized for \(x=0.07\) and \(x=0.10\). Whereas the stabilization of β-phase takes place at \(x=0.13\) for Ca\(^{2+}\) substituted system and \(x=0.17\) for Ba\(^{2+}\) substituted system. In Sn\(^{4+}\) substituted system the stabilization of α-phase takes place only at \(x=0.07\) and β-phase is stabilized for \(0.10 \leq x \leq 0.17\). Whereas for Mn\(^{4+}\) substituted system α-phase does not exist at all and only the β-phase is stabilized for \(0.07 \leq x \leq 0.17\). In all the four substituted systems the stabilization of high temperature γ-phase takes place for \(x=0.20\) and \(x=0.30\).

From DTA results, three principal transitions α↔β, β↔γ and γ'↔γ are detected for BICAVOX and BISNVOX systems. For BIBAVOX system, apart from α↔β and β↔γ transition a new type of transition i.e. α↔γ is observed at temperatures 385 and 403 °C for \(x=0.10\) and \(x=0.13\) respectively. Whereas in BIMNVOX system only β↔γ and γ'↔γ transitions are observed. The existence of such transitions is also evidently proved by the XRPD patterns and Arrhenius plots of conductivity.

The values of conductivity calculated at 300 °C from Arrhenius plots for all these substituted system follow the order BICAVOX \((\sigma_{300\degree C}= 3.27 \times 10^{-4} \text{ S.cm}^{-1}) >\)
BISNVOX ($\sigma_{300^\circ C} = 5.03 \times 10^{-5}$ S.cm$^{-1}$) > BIBAVOX ($\sigma_{300^\circ C} = 4.45 \times 10^{-5}$ S.cm$^{-1}$) > BIMNVOX ($\sigma_{300^\circ C} = 2.47 \times 10^{-5}$ S.cm$^{-1}$) i.e. Ca$^{2+}$ doped system has the highest ionic conductivity among all the four substituted systems. The lower temperature conductivities for BIBAVOX, BISNVOX and BIMNVOX system had maxima for $x=0.17$ which is in the composition range of the stabilized $\beta$–phase. This is likely due to the increased ordering of vacancies, resulting from the long–term stabilization of $\alpha$–and $\beta$–polymorphs. While for the BICAVOX system, the maximum conductivity was observed at $x=0.17$, which is in the region of stabilized $\gamma$-phase.

The AC impedance plots show that the conductivity exhibited by all these electrolyte materials is mainly due to the grain contribution to the total ionic conductivity which is evident in the enhanced short range diffusion of oxide-ion vacancies in the grains with increasing temperature.

In the end it can be concluded that the new oxide–ion conductors prepared in this study will be potential candidates for IT–SOFC applications as they exhibit satisfactory structural and electrical properties.