Chapter-7

SUMMARY AND FUTURE SCOPE

7.1 Summary

This thesis aimed to develop a superior oxide-ion electrolyte which can operate at lower temperatures. We have successfully established the role of dielectric relaxation in superior oxide-ion conductivities for SOFCs. Dielectric leakage or Relaxor-like characteristics of ferroelectrics or high k dielectric materials reveal a substantial temperature and frequency dependence in the maximum of both real and imaginary parts of dielectric permittivity. However, relaxors show not only particular and intriguing behaviours in the dielectric response but also show promising activity in fast-ion conduction to be applied as an oxide-ion conductor for the application in solid oxide fuel cells (SOFCs), the relaxor nature of high k dielectricity and higher polarizability of oxygen-vacant doped materials, seems to play a directive role in providing superior oxide-ion transport throughout the lattice at a temperature close to dielectric relaxation temperatures. In this thesis, we have found that the high polarizability of doped ion couple with high k dielectric relaxation (high dielectric leakage) can generate superior oxide-ion conduction near T_m (The temperature of the maximum *dielectric permittivity*). We have presented the proof of concept through the exploration of novel structures coupled with doping of Ti^{4+} & Ge^{4+} ions into $KTaO_3$ lattice, Bi^{3+} and Gd^{3+} ions into ZrO_2 lattice, K & Ga ions into $BaZrO_3$ & $SrTiO_3$ lattice, to stabilize cubic phase and found that the synergistic interaction by introducing a secondary substituent enhances the oxide-ion vacancy transport within the percolation limit of ion transport inside the host structure at lower temperatures.

Chapter 1 deals with a brief introduction of the current energy crisis, global warming and other environmental issues that can be answered using SOFCs as an alternative power source. A brief history of fuel cells and types of fuel cells are also included. A detailed review of oxide-ion electrolytes utilised in SOFCs and that limits the application of SOFCs is also presented.

Chapter 2 deals with novel preparation methods for the material synthesis and presents the know-how and theoretical background of characterisation techniques utilised in the dissertation.

In Chapter 3, the Novel high κ dielectric/ferroelectric $KTaO_3$ perovskite structure is envisaged as a host lattice to develop a superior oxide-ion electrolyte. The simultaneous substitution of smaller cations such as Ti^{4+} and Ge^{4+} on Ta site was carried out to create an oxide-ion vacancy in the host lattice. The simultaneous substitution of Ti and Ge developed lossy nature of High κ relaxor dielectricity or polarisation in $KTa_{0.4}Ti_{0.3}Ge_{0.3}O_{2.7,}$ resulting in high oxide-ion conductivity at elevated temperatures (Oxide-ion conductivity $\sigma_o > 10^{-2}$ s/cm, $T \geq 550^oC$). The maxima of the Dielectric constant or highest dielectric constant were found at ~ 5300 at applied frequency 20 kHz at 650^oC, and The T_m was varying or decreasing with increasing applied frequency. This linear decrease of T_m from 650^oC to 550^oC from 20 kHz to 100 kHz of applied frequency confirms the relaxor/leaking nature of high κ dielectric behaviour $KTa_{0.4}Ti_{0.3}Ge0.3O_{2.7}$. The high oxide-ion conductivity of $KTa_{0.4}Ti_{0.3}Ge_{0.3}O_{2.7}$ was observed in coherence with the T_m variation with the applied frequency, establishing the high κ dielectric in accelerating the motion of oxide-ion vacancies within the percolation limit inside the host crystalline structure.

In Chapter 4, The main was to overcome the low ionic conductivity issues of $BaZrO_3$ based materials at elevated temperature, the simultaneous doping of smaller Ga on Zr site and K on Ba site was employed here to create higher concentration of oxide-ion vacancies for the realisation of superior conductivities. The simultaneous substitution of K and Ga created the oxygen vacancies type point defects resulting in higher ionic conductivity $\sim 10^{-2}$ S/cm above 650^oC. The conductivity represented here for $Ba_{0.8}K_{0.2}Zr_{0.8}Ga_{0.2}O_{2.8}$ sample is superior or equivalent to the conductivity obtained for yttria stabilised zirconia; a well-known ceramic oxide-ion electrolyte.

In Chapter 5, the simultaneous doping of smaller Ga on Ti site and K on Sr site were employed here to create a higher concentration of oxide-ion vacancies to realise superior conductivities. The simultaneous substitution of K and Ga devised the oxygen-vacancies type point defects resulting in higher ionic conductivity ~10^{-2} S/cm above 650^{o}C, almost similar to $Ba_{0.8}K_{0.2}Zr_{0.8}Ga_{0.2}O_{2.8,}$ which was also comparable to already known oxide-ion electrolytes.

In Chapter 6, the cubic phase of ZrO_2 was stabilised with simultaneous substitution of Bi and Gd. The effect of co-doping on oxide-ion conductivity of $Zr_{1-x-y}Bi_xGd_yO_{2-\delta}$ was studied to develop a superior electrolyte separator for SOFCs. Up to 30% Gd and 20% Bi were simultaneously substituted in cubic ZrO_2 lattice ($Zr_{1-x-y}Gd_xBi_yO_{2-\delta}$, $x+y\leq0.4$, $x \leq 0.3$ and $y \leq 0.2$). The powder XRD and EDX measurements confirm the material's purity and composition. The Raman spectroscopy study confirmed the formation of oxygen vacant Gd/Bi co-doped cubic Zirconia lattice. With the incorporation of Bi^{3+} and Gd^{3+} ions, the cubic $Zr_{1-x-y}Bi_xGd_yO_{2-\delta}$ phase showed relaxor type high κ dielectric behaviour (ἐ = 9725 at 600^{o}C at applied frequency 20 kHz for $Zr_{0.6}Bi_{0.2}Gd_{0.2}O_{1.8}$) with T_m approaching to 600^{o}C. High polarizability of Bi^{3+} ion coupled with synergistic interaction of Bi and Gd in the host ZrO_2 lattice seems to create the more labile oxide-ion vacancies that enable superior oxide-ion transport resulting in high oxide-ion conductivity (σ_o> 10^{-2}s/cm, T > 500^{o}C for $Zr_{0.6}Bi_{0.2}Gd_{0.2}O_{1.8}$) at relatively lower temperatures.

7.2 Future Scope

The present study also opens the doors for the employment of novel structural design of materials to generate active oxide-ion vacancies and develop superior ionic conductors. The material can also be explored in a high moisture-rich or humidified environment for its applications as a protonic conductor for ceramic fuel cells and hydrogen separating membrane formations.

Further, we can see that relaxor dielectric is the crucial fundamental feature that regulates the oxide-ion conductivities of the sample. We have already shown that as transition temperature (T_m) approaches, the conductivity maximises in the samples. These unique features can be used as directive principles to develop new materials for the oxide-ion electrolytes for SOFCs. Nonetheless, more studies are required to determine the applicability of the materials as an oxide-ion electrolyte for the production of IT-SOFCs