Dedicated to

My Parents

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It is certified that the work contained in the thesis titled ***“Investigation of the Role of dielectric relaxation in resulting superior conductivities of oxide ion electrolytes for Solid Oxide Fuel Cells”*** by ***Akanksha Yadav*** has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

It is further certified that the student has fulfilled all the requirements of the comprehensive examination, candidacy and SOTA for the award of Ph.D. Degree.

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DECLARATION BY THE CANDIDATE

I, ***Akanksha Yadav***, certify that the work embodied in this thesis is my own bonafide work and carried out by me under the supervision of ***Dr. Preetam Singh*** from ***July 2016*** to ***April 2022***, at the ***Department of Ceramic Engineering***, Indian Institute of Technology (BHU), Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma.

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LIST OF ABBREVIATIONS

T_m	Transition Temperature
CNG	Compressed natural gas
SOFCs	Solid Oxide Fuel Cells
YSZ	Yttria-Stablized Zirconia
AFCs	Alkaline Fuel Cells
PAFCs	Phosphoric Acid Fuel Cells
PEMFCs	Proton Exchange Membrane Fuel Cells
MCFCs	Molten Carbonate Fuel Cells
IT-SOFCs	Intermediate Temperature- Solid Oxide Fuel Cells
ScSZ	Sc_2O_3 stabilized ZrO_2
SDC	Samarium doped ceria
OCV	open circuit voltage
PZT	Lead Zirconate Titanate
XRD	Powder X-Ray Diffraction
FESEM	Field Emission Scanning Electron Microscope
HR-TEM	High-Resolution Transmission Electron Microscopy
TEM	transmission electron microscope
SAD	selected area diffraction
EDAX	Energy Dispersive X-Ray Spectroscopy
DSC	Differential Scanning Calorimetry
FTIR	Fourier Transform Infrared Spectroscopy
EIS	Electrochemical Impedance Spectroscopy

PREFACE

Fuel cells are the electrochemical devices capable of continuously converting the chemical energy stored in a fuel such as hydrogen or methane to electricity. Fuel cell technologies can be employed to gradually reduce fossil fuel dependency and environmental impact compared to conventional combustion-based power generation technologies. Solid oxide fuel cells (SOFCs) use ceramic oxide-ion or proton-conducting electrolytes as separators to electrochemically connect the fuel (Hydrogen or Methane) to oxidant (air or oxygen) to produce electricity. SOFC operates at higher temperatures to avoid the ohmic losses generated due to lower ionic conductivities of electrolyte separators. One of the key approaches to lowering the operating temperature of solid oxide fuel cells (SOFCs) is to develop novel electrolyte materials with superior ionic conductivities, thermo-mechanical properties, and low processing temperature compared to the well-known ones perovskite and fluorite based oxide ion conductors. This thesis focuses on the synthesis of oxide-ion conductors and establishing the role of high κ dielectric in accelerating the motion of oxide-ion vacancies. Novel materials were synthesized employing the solid-state and sol-gel auto-combustion method. Samples were characterized structurally (XRD), morphologically (SEM, TEM-EDAX), and thermally (TGA, DSC) thoroughly. Spectroscopy studies (Impedance, Raman, FTIR) were also deliberated to understand the transport properties of the samples.

Perovskite oxides with anionic vacancies (inherent or created by doping) perform as oxide ion conductors in a dry atmosphere at higher temperatures and proton conductors in a hydrated atmosphere at lower operating temperatures. Novel high κ dielectric/ferroelectric $KTaO_3$ perovskite structure is envisaged here as a host lattice to develop a superior oxide-ion electrolyte. The simultaneous substitution of Ti and Ge developed lossy nature of high κ relaxor dielectricity or polarization 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 ≥ 550°C). The maxima of the dielectric constant or highest dielectric constant were found at ~ 5300 at applied frequency 20 kHz at 650°C, and T_m was varying or decreasing with increasing applied frequency. This linear decrease of T_m from 650°C to 550°C from 20 kHz to 100 kHz of applied frequency confirms the relaxor/leaking nature of high κ dielectric behaviour of $KTa_{0.4}Ti_{0.3}Ge_{0.3}O_{2.7}$. The high oxide-ion conductivity of the samples was observed in correlation with the T_m variation with the applied frequency establishing the role of high κ dielectric in accelerating the motion of oxide-ion vacancies within the percolation limit inside the host crystalline structure. Similarly, doped $BaZrO_3$ and $SrTiO_3$ are the other perovskites explored in this thesis. To overcome the low ionic conductivity issues of $BaZrO_3$ & $SrTiO_3$ based materials at elevated temperatures, the simultaneous doping of smaller Ga on Zr and Ti site and K on Ba and Sr site respectively in $BaZrO_3$ and $SrTiO_3$ was employed here to create a higher concentration of oxide-ion vacancies to realize superior oxide-ion conductivities. The simultaneous substitution of K and Ga created the oxygen vacancies type point defects resulting in higher ionic conductivity ~10^{-2} S/cm above 650°C. The conductivity represented here for $Ba_{0.8}K_{0.2}Zr_{0.8}Ga_{0.2}O_{2.8}$ and $Sr_{0.8}K_{0.2}Ti_{0.8}Ga_{0.2}O_{2.8}$ sample is superior or equivalent to the conductivity obtained for the yttria-stabilized zirconia; a well known ceramic oxide-ion electrolyte.

To develop a superior alternative to YSZ, cubic phase of ZrO_2 was stabilized with simultaneous doping of Bi and Gd in the form of $Zr_{1-x-y}Bi_xGd_yO_{2-\delta}$ and was proposed as an oxide-ion conductor to be an electrolyte for IT-SOFC. ZrO_2 is a key constituent in the perovskite structure, and ZrO_6 octahedra act as a central point in providing high dielectric and ferroelectric constant in PZT-based perovskite structures. With the incorporation of Bi^{3+} and Gd^{3+} ions, in conjunction with lone pairs of Bi, the cubic $Zr_{1-x-y}Bi_xGd_yO_{2-\delta}$ phase showed relaxor type high κ dielectric behaviour (έ= 9725 at 600 °C at applied frequency 20 kHz) with

T_m approaching to 600°C. Synergistic interaction of Bi and Gd in the host ZrO_2 lattice also seems to create the more labile or movable oxide ion vacancies that enable superior oxide-ion transport resulting in high oxide ion conductivity ($\sigma_o > 10^{-2}$ s/cm, T > 500°C) at relatively lower temperatures.

Therefore, in this thesis, I conclude that dielectric relaxation is the crucial fundamental feature that plays important role in the oxide-ion conductivities of the sample. I have already shown that as T_m approaches, the conductivity maximizes in the samples. These unique features can be used as directive principles to develop new superior oxide-ion electrolytes for SOFCs.