

*Dedicated to*

*My Parents*



भारतीय  
प्रौद्योगिकी  
संस्थान  
काशी हिन्दू विश्वविद्यालय

INDIAN  
INSTITUTE OF  
TECHNOLOGY  
BANARAS HINDU UNIVERSITY

## CERTIFICATE

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.

**(Dr. Preetam Singh)**  
**Supervisor**  
**Assistant Professor,**  
**Department of Ceramic Engineering,**  
**Indian Institute of Technology (BHU),**  
**Varanasi - 221005, (U.P.), India**

**(Prof. Ram Pyare)**  
**Co-Supervisor**  
**Professor,**  
**Department of Ceramic Engineering,**  
**Indian Institute of Technology (BHU),**  
**Varanasi - 221005, (U.P.), India**

**Head of Department**  
**Department of Ceramic Engineering**  
**Indian Institute of Technology (BHU),**  
**Varanasi - 221005, (U.P.), India**



## 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.

I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not willfully copied any other's work, paragraphs, text, data, results, *etc.*, reported in journals, books, magazines, reports dissertations, thesis, *etc.*, or available at websites and have not included them in this thesis and have not cited as my own work.

Date:

Place: IIT (BHU), Varanasi

Signature of the student

(*Akanksha Yadav*)

## CERTIFICATE BY THE SUPERVISOR

It is certified that the above statement made by the student is correct to the best of my/our knowledge.

**Dr. Preetam Singh**  
Supervisor  
Assistant Professor,  
Department of Ceramic Engineering,  
Indian Institute of Technology (BHU),  
Varanasi - 221005, (U.P.), India

**Prof. Ram Pyare**  
Co-Supervisor  
Professor,  
Department of Ceramic Engineering,  
Indian Institute of Technology (BHU),  
Varanasi - 221005, (U.P.), India

**Head of Department**  
Department of Ceramic Engineering  
Indian Institute of Technology (BHU),  
Varanasi - 221005, (U.P.), India



## COPYRIGHT TRANSFER CERTIFICATE

**Title of the Thesis:** *Investigation of Role of dielectric relaxation resulting in conductivities of oxide ion electrolytes for Solid Oxide Fuel Cells*

**Name of the Student:** *Akanksha Yadav*

### Copyright Transfer

The undersigned hereby assigns to the Indian Institute of Technology (Banaras Hindu University) Varanasi all rights under copyright that may exist in and for the above thesis submitted for the award of the “*DOCTOR OF PHILOSOPHY*”.

Date:

Place: IIT (BHU), Varanasi

Signature of the Student

*(Akanksha Yadav)*

**Note:** However, the author may reproduce or authorize others to reproduce material extracted verbatim from the thesis or derivative of the thesis for the author's personal use provided that the source and the Institute's copyright notice are indicated.

## **Acknowledgements**

The journey of PhD has been a turning point of my life, and it would not be possible without the constant support, assistance and guidance that I have received from countless people. I would like to take this opportunity to acknowledge and appreciate those people who have given their valuable time during my PhD.

I am indebted to my thesis supervisor Dr. Preetam Singh for his constant monitoring, enthusiastic encouragement, continued guidance, and unconditional support throughout my PhD journey. I always admire his knowledge of the subject, his unconventional thinking, and enthusiastic nature for research. His ingenious approach to research is a source of inspiration, and this approach is reflected in his simple but clear writing style, which I want to carry forward in my career. I have been fortunate enough to be part of his group. His suggestions and advises will always be beneficial in life, whether it is academic or non academic. I am very thankful to you sir for being a mentor academically as well as philosophically and wish to continue to seek this mentorship for future life too.

I am thankful to my RPEC members, Dr. J. V. Tirkey, Dr. M. R. Manjhi, Dr. Ram Pyare, for their knowledgeable, motivational and umpteen suggestions throughout this research work.

I want to express my gratitude towards Ex-Head of Department, Prof. D.Kumar, Head of Department Prof. Vinay Kumar Singh for providing me required facilities of the department. I also wish to thank all the faculty members of the Department of Ceramic Engineering, Prof. D. Kumar, Prof. Om Prakash, Prof. S.P. Singh, Prof. Ram Pyare, Prof. Vinay Kumar Singh, Dr. Anil Kumar, Dr. M. R. Majhi, Dr. P. K. Roy, Dr. Ashutosh Dubey, Dr. Santanu Das, Dr. Preetam Singh, Dr. Imteyaz Ahmed, Dr. Sudama Singh, Dr. R.K. Chaturvedi, Dr. Akanksha Dwivedi, Dr. Kalyani Mohanta, for their motivation, selfless support and suggestions during course work as well as my whole Ph.D. time.

I would also like to thank Prof. Rajiv Prakash for providing experimental facilities during the entire course of research work at CIFC, IIT (BHU). Along with that I am also thankful to all the staff at CIFC, IIT(BHU). I am also grateful to Prof. Goodenough, Department of Mechanical Engineering, University of Texas, UT Austin USA and Dr. T. Maiyalagan Department of Chemistry, SRM University Chennai, for their valuable discussions over the scientific work.

I would like to extend thanks to Dr. Asha Gupta, Department of Chemistry IIT(BHU) for providing lab facility at the time of crisis. I also gratefully acknowledge the financial support of the Ministry of Education, India (formally known as Ministry of Human Resource and Development; MHRD, India).

I am also thankful to all non-teaching staff, Mr. Shailendra, Mr. Pawan, Mr. Prasant , Mr. K. K. Maurya, (office staff) Mr. Ashish Tripathi, Mr. Bhagmal Ji, Mr. Mansa Ram (all Technical and workshop staff) of the Department of Ceramic Engineering for their kind cooperation. I am very thankful to the labmates Rakesh, Neeraj, Krishna, Neeraj, Himanshu, Arhan, Vandna for cooperating and maintaining the lab culture. I wish to express my sincere gratitude to all those who have extended their helping hands in various ways during my tenure at the Indian Institute of Technology (Banaras Hindu University), Varanasi, India. I am also thankful for the negative energies which teaches me life lessons and help me to grow.

I am highly obliged to my family, Maa Mrs. Munni Devi, Papa Mr.Gyan Singh Yadav, beloved brothers Akash & Ayush and my Husband, Himanshu Pandey, as without their continuing support, love, laughter, and their motivation to keep me coherent made this project possible especially during many rough patches of time.I would also include my In-laws in the list for being understanding and supportive. I would like to mention my friends Rashika, Gaurav, Tripti, Taresh, Mahima, Vandna, Deepti, Yamini, Monika, Khyati, Nikita etc for having that emotional and motivational support during the tenure. Lastly, I want to thank almighty God for all positive opportunities and negative situations which prepare me to handle situations for the future life.

## **Table of Contents**

List of Figures.....	<i>xiii</i>
List of Tables .....	<i>xvi</i>
List of Abbreviations .....	<i>xvii</i>
Perface.....	<i>xviii</i>

### **Chapter 1 Introduction**

1.1 Energy Crisis and Global Warming.....	1
1.2 Historical Background.....	3
1.3 Types of fuel cells .....	5
1.3.1 Alkaline Fuel Cells .....	5
1.3.2 Phosphoric Acid Fuel Cells .....	6
1.3.3 Proton Exchange Membrane Fuel Cells .....	7
1.3.4 Molten Carbonate Fuel Cells .....	9
1.3.5 Solid Oxide Fuel Cells.....	10
1.4 SOFC Design .....	13
1.5 Key Challenges of SOFCs.....	15
1.6 Fluorite Electrolytes.....	16
1.6.1 Stablized ZrO <sub>2</sub> .....	17
1.6.2 Doped Ceria .....	18
1.6.3 Bi <sub>2</sub> O <sub>3</sub> -based Electrolyte.....	19
1.7 Perovskite Electrolyte .....	20
1.7.1 LaGaO <sub>3</sub> based electrolyte .....	21
1.7.2 NBT based Electrolyte .....	22
1.7.3 Other Electrolyte .....	23
1.8 Scope of thesis.....	25
References.....	26

### **Chapter 2**

Experimental Techniques .....	39
2.1 Overview .....	39
2.2 Synthesis Technique.....	39
2.2.1 Solid state reaction synthesis route.....	39
2.2.2 Sol-Gel Auto Combustion Synthesis .....	40
2.2.3 Palletization .....	41

<b>2.3 Material Characterization Techniques .....</b>	<b>42</b>
<b>2.3.1 X-Ray Diffraction.....</b>	<b>43</b>
<b>2.3.2 Phase Formation and Crystal Structure Studies by Powder XRD .....</b>	<b>44</b>
<b>2.3.3 Field Emission Scanning Electron Microscope .....</b>	<b>45</b>
<b>2.3.4 High-Resolution Transmission Electron Microscopy(HRTEM).....</b>	<b>45</b>
<b>2.3.5 Energy Dispersive X-RAY Spectroscopy(EDX) .....</b>	<b>47</b>
<b>2.3.6 Thermogravimetric Analysis(TGA) .....</b>	<b>48</b>
<b>2.3.7 Differential Scanning Calorimetry (DSC).....</b>	<b>48</b>
<b>2.3.8 Raman Spectroscopy .....</b>	<b>49</b>
<b>2.3.9 FTIR Spectroscopy .....</b>	<b>50</b>
<b>2.3.10 Electrochemical Impedance Spectroscopy (EIS) .....</b>	<b>50</b>
<b>2.3.11 Conductivity Measurement Using EIS .....</b>	<b>53</b>
<b>References.....</b>	<b>54</b>

### Chapter 3

<b>KTaO<sub>3</sub> Based Perovskite material for Oxide Ion Electrolyte for SOFCs .....</b>	<b>55</b>
<b>3.1 Introduction.....</b>	<b>55</b>
<b>3.2 Material Synthesis &amp; Characterization .....</b>	<b>55</b>
<b>3.3 Thermal Study.....</b>	<b>56</b>
<b>3.4 Crystal Structure Study.....</b>	<b>58</b>
<b>3.5 SEM/EDX Study .....</b>	<b>60</b>
<b>3.6 EIS Study .....</b>	<b>61</b>
<b>3.7 Conclusion .....</b>	<b>66</b>
<b>References.....</b>	<b>67</b>

### Chapter 4

<b>Doped BaZrO<sub>3</sub> as oxide ion conductor.....</b>	<b>69</b>
<b>4.1 Introduction.....</b>	<b>69</b>
<b>4.2 Material Synthesis and Characterization .....</b>	<b>70</b>
<b>4.3 Result and Discussion .....</b>	<b>71</b>
<b>4.3.1 XRD Study .....</b>	<b>71</b>
<b>4.3.2 Thermal Study.....</b>	<b>77</b>
<b>4.3.3 SEM Study .....</b>	<b>78</b>
<b>4.3.4 TEM Study.....</b>	<b>79</b>

4.3.5 Impedance Study.....	81
4.4 Conclusion.....	86
References.....	87

## Chapter 5

Study of SrTiO <sub>3</sub> based Pervoskite Material for developing superior oxide-ion electrolyte .....	89
5.1 Introduction.....	89
5.2 Material Synthesis and characterization .....	89
5.3 Crystal Structure Study.....	91
5.4 Thermal Study.....	94
5.5 SEM Study .....	95
5.6 Impedance Study.....	96
5.8 Conclusion .....	99
References.....	100

## Chapter 6

Bi & Gd Co-Substituted Zirconia based Oxide Ion Conductor.....	103
6.1 Introduction.....	103
6.2 Material Synthesis .....	105
6.3 Material Characterization.....	105
6.4 Crystal Structure Analysis .....	106
6.5 SEM/EDX Study .....	109
6.6 Raman Spectroscopy Analysis .....	111
6.7 Impedance Study.....	112
6.8 Thermal Study.....	118
6.9 Conclusion .....	123
References.....	125

## Chapter 7

Summary and Future Scope .....	131
7.1 Summary.....	131
7.2 Future Scope .....	134

## LIST OF FIGURES

Figure No.	Figure description	Page No.
Figure 1.1	Energy Consumption World Wide 2000 to 2018, with a forecast till 2050* (in extra joules)	1
Figure 1.2	Electricity Generation by Source	2
Figure 1.3	Comparison of efficiencies of conventional power generation & fuel cells.	3
Figure 1.4	Alkaline fuel cell	6
Figure 1.5	Phosphoric Acid & PEM fuel cell	9
Figure 1.6	Molten carbonate fuel cell	10
Figure 1.7	Solid Oxide Fuel Cell	13
Figure 1.8	Tubular Design of SOFCs	14
Figure 1.9	Planar Design of SOFCs	14
Figure 1.10	Fluorite structure	16
Figure 1.11	Perovskite Structure	20
Figure 2.1	Solid State Synthesis Route	40
Figure 2.2	Sol-Gel Auto Combustion	41
Figure 2.3	Pelletization Steps	42
Figure 2.4	Characterization techniques used	42
Figure 2.5	Demonstration for Bragg's Law	43
Figure 2.6	Interaction of electrons with sample	47
Figure 2.7	Nyquist Plot for ionic solids	52
Figure 2.8	Conductivity Test station	53
Figure 3.1	Thermogravimetric analysis (TGA) curve of $\text{KTa}_{0.4}\text{Ti}_{0.3}\text{Ge}_{0.3}\text{O}_{2.7}$	57
Figure 3.2	FT-IR spectra of $\text{KTa}_{0.4}\text{Ti}_{0.3}\text{Ge}_{0.3}\text{O}_{2.7}$	57
Figure 3.3	Powder XRD pattern (a) $\text{KTa}_{0.6}\text{Ti}_{0.4}\text{O}_{2.8}$ (b) $\text{KTa}_{0.6}\text{Ge}_{0.4}\text{O}_{2.8}$ and (c) $\text{KTa}_{0.4}\text{Ti}_{0.3}\text{Ge}_{0.3}\text{O}_{2.7}$	59
Figure 3.4	Rietveld refined powder XRD profile of (a) $\text{KTa}_{0.6}\text{Ti}_{0.4}\text{O}_{2.8}$ (b) $\text{KTa}_{0.6}\text{Ge}_{0.4}\text{O}_{2.8}$ and (c) $\text{KTa}_{0.4}\text{Ti}_{0.3}\text{Ge}_{0.3}\text{O}_{2.7}$	60

<b>Figure 3.5</b>	SEM image $\text{KTa}_{0.4}\text{Ti}_{0.3}\text{Ge}_{0.3}\text{O}_{2.7}$ (a) Powder (b) top view of the pellet (c) Cross-section of the pellets and (d) Image of EDX spectra	61
<b>Figure 3.6</b>	Arrhenius plot of (a) various compositions, (b) $\text{KTa}_{0.4}\text{Ti}_{0.3}\text{Ge}_{0.3}\text{O}_{2.7}$ in different mediums, (c) comparison of existing intermediate temperature Oxide-ion electrolytes in air	64-65
<b>Figure 3.7</b>	Cole-Cole plot of $\text{KTa}_{0.4}\text{Ti}_{0.3}\text{Ge}_{0.3}\text{O}_{2.7}$ at $600^\circ\text{C}$ . Inset shows the plot between 30 kHz to 20Hz frequencies.	65
<b>Figure 3.8</b>	The dielectric constant of $\text{KTa}_{0.4}\text{Ti}_{0.3}\text{Ge}_{0.3}\text{O}_{2.7}$ at different temperatures and frequencies.	66
<b>Figure 4.1</b>	Photograph of synthesized powder (off-white colour) & $\text{BaZrO}_3$	71
<b>Figure 4.2</b>	Powder XRD pattern (a) $\text{BaZrO}_3$ (b) $\text{Ba}_{0.9}\text{K}_{0.1}\text{Zr}_{0.9}\text{Ga}_{0.1}\text{O}_{2.9}$ (K10G10) (c) $\text{Ba}_{0.85}\text{K}_{0.15}\text{Zr}_{0.85}\text{Ga}_{0.15}\text{O}_{2.85}$ (K15G15) (d) $\text{Ba}_{0.8}\text{K}_{0.2}\text{Zr}_{0.8}\text{Ga}_{0.2}\text{O}_{2.8}$ (K20G20) (e) $\text{Ba}_{0.75}\text{K}_{0.25}\text{Zr}_{0.75}\text{Ga}_{0.25}\text{O}_{2.75}$ (K25G25)	72
<b>Figure 3.3</b>	Systematic peak shift of (011) plane of $\text{Ba}_{1-x}\text{K}_x\text{Zr}_{1-x}\text{Ga}_x\text{O}_{3-x}$ ( $x = 0, 0.1, 0.15, 0.2$ and $0.25$ ) samples with doping.	73
<b>Figure 4.4(a)</b>	Rietveld refined powder XRD profile of $\text{Ba}_{0.9}\text{K}_{0.1}\text{Zr}_{0.9}\text{Ga}_{0.1}\text{O}_{2.9}$	74
<b>Figure 4.4(b)</b>	Rietveld refined powder XRD profile of $\text{Ba}_{0.85}\text{K}_{0.15}\text{Zr}_{0.85}\text{Ga}_{0.15}\text{O}_{2.85}$	75
<b>Figure 4.4(c)</b>	Rietveld refined powder XRD profile of $\text{Ba}_{0.8}\text{K}_{0.2}\text{Zr}_{0.8}\text{Ga}_{0.2}\text{O}_{2.8}$	75
<b>Figure 4.4(d)</b>	Rietveld refined powder XRD profile of $\text{Ba}_{0.75}\text{K}_{0.25}\text{Zr}_{0.75}\text{Ga}_{0.25}\text{O}_{2.75}$	76
<b>Figure 4.5</b>	Thermogravimetric analysis (TGA) & DSC curve of $\text{Ba}_{0.8}\text{K}_{0.2}\text{Zr}_{0.8}\text{Ga}_{0.2}\text{O}_{2.8}$	78
<b>Figure 4.6</b>	SEM image $\text{Ba}_{0.8}\text{K}_{0.2}\text{Zr}_{0.8}\text{Ga}_{0.2}\text{O}_{2.8}$ (a) Powder (b) top view of the pellet (c) Cross-section of the pellets and (d) Image of EDX spectra	79
<b>Figure 4.7</b>	(a) & (b) TEM image Powder $\text{Ba}_{0.8}\text{K}_{0.2}\text{Zr}_{0.8}\text{Ga}_{0.2}\text{O}_{2.8}$ (c) SAED pattern from $\text{Ba}_{0.8}\text{K}_{0.2}\text{Zr}_{0.8}\text{Ga}_{0.2}\text{O}_{2.8}$ (d) HRTEM of $\text{Ba}_{0.8}\text{K}_{0.2}\text{Zr}_{0.8}\text{Ga}_{0.2}\text{O}_{2.8}$ Showing (011) planes (e) Elemental mapping of the $\text{Ba}_{0.8}\text{K}_{0.2}\text{Zr}_{0.8}\text{Ga}_{0.2}\text{O}_{2.8}$	80
<b>Figure 4.8</b>	Arrhenius plot for different composition of K and Ga substituted $\text{BaZrO}_3$ i.e. (i) $\text{Ba}_{0.9}\text{K}_{0.1}\text{Zr}_{0.9}\text{Ga}_{0.1}\text{O}_{2.9}$ (K10G10) (ii) $\text{Ba}_{0.85}\text{K}_{0.15}\text{Zr}_{0.85}\text{Ga}_{0.15}\text{O}_{2.85}$ (K15G15) (iii)	82

	$Ba_{0.8}K_{0.2}Zr_{0.8}Ga_{0.2}O_{2.8}$ (K20G20) (iv) $Ba_{0.75}K_{0.25}Zr_{0.75}Ga_{0.25}O_{2.74}$ (K25G25)	
<b>Figure 4.9</b>	Arrhenius plot of $Ba_{0.8}K_{0.2}Zr_{0.8}Ga_{0.2}O_{2.8}$ (BKGZO) in different medium	83
<b>Figure 4.10</b>	comparison of ionic conductivities of existing intermediate temperature Oxide-ion electrolytes in the air	83
<b>Figure 4.11</b>	Cole-Cole plot of $Ba_{0.8}K_{0.2}Zr_{0.8}Ga_{0.2}O_{2.8}$ at(a) 400°C (b) 500°C	85-86
<b>Figure 5.1</b>	Powder XRD pattern (a) $SrTiO_3$ (b) $Sr_{0.9}K_{0.1}Ti_{0.9}Ga_{0.1}O_{2.9}$ (SK10G10) (c) $Sr_{0.85}K_{0.15}Ti_{0.85}Ga_{0.15}O_{2.85}$ (SK15G15) (d) $Sr_{0.8}K_{0.2}Ti_{0.8}Ga_{0.2}O_{2.8}$ (SK20G20) (e) $Sr_{0.75}K_{0.25}Ti_{0.75}Ga_{0.25}O_{2.75}$ (SK25G25)	91
<b>Figure 5.2(a)</b>	Rietveld refined powder XRD profile of $Sr_{0.9}K_{0.1}Ti_{0.9}Ga_{0.1}O_{2.9}$	92
<b>Figure 5.2(b)</b>	Rietveld refined powder XRD profile of $Sr_{0.8}K_{0.2}Ti_{0.8}Ga_{0.2}O_{2.8}$	92
<b>Figure 5.3</b>	Thermogravimetric analysis (TGA) of $Sr_{0.8}K_{0.2}Ti_{0.8}Ga_{0.2}O_{2.8}$	94
<b>Figure 5.4</b>	SEM image $Sr_{0.8}K_{0.2}Ti_{0.8}Ga_{0.2}O_{2.8}$ (a) Powder (b) pellet (c) EDX image of pallet	95
<b>Figure 5.5</b>	Arrhenius plot of Various compositions $Sr_{1-x}K_xTi_{1-y}Ga_yO_{3-\delta}$	98
<b>Figure 5.6</b>	Comparison of ionic conductivities of existing intermediate Oxide-ion electrolytes in the air	98
<b>Figure 6.1</b>	Powder XRD pattern (i) $Zr_{0.6}Bi_{0.2}Gd_{0.2}O_{1.8}$ , (ii) $Zr_{0.6}Bi_{0.15}Gd_{0.25}O_{1.8}$ , (iii) $Zr_{0.65}Bi_{0.15}Gd_{0.2}O_{1.825}$ , (iv) $Zr_{0.7}Bi_{0.15}Gd_{0.15}O_{1.85}$ , and (v) $Zr_{0.6}Bi_{0.10}Gd_{0.30}O_{1.8}$	107
<b>Figure 6.2</b>	Rietveld refined powder XRD profile of (i) $Zr_{0.6}Bi_{0.2}Gd_{0.2}O_{1.8}$ (ii) $Zr_{0.6}Bi_{0.10}Gd_{0.30}O_{1.8}$	108
<b>Figure 6.3</b>	SEM image $Zr_{0.6}Bi_{0.2}Gd_{0.2}O_{1.8}$ (a) Powder (b) Top view of the pellet (c) Cross-section of the pallets and (d) EDX image of pallet	110
<b>Figure 6.4</b>	Vacancy mapping through Bi lone pair in cubic fluorite structure	111
<b>Figure 6.5</b>	Raman spectra of (a) monoclinic $ZrO_2$ and (b) Gd-Bi co-doped cubic Zirconia ( $Zr_{0.6}Bi_{0.2}Gd_{0.2}O_{1.8}$ )	112
<b>Figure 6.6</b>	Arrhenius plot of various compositions	115
<b>Figure 6.7</b>	Arrhenius plot of $Zr_{0.6}Bi_{0.2}Gd_{0.2}O_{1.8}$ (ZBGO) in different medium	116

<b>Figure 6.8</b>	Cole-Cole plot of $Zr_{0.6}Bi_{0.2}Gd_{0.2}O_{1.8}$ at 500°C	116
<b>Figure 6.9</b>	Arrhenius plot of comparison of existing intermediate temperature Oxide-ion electrolytes in air	117
<b>Figure 6.10</b>	Powder XRD pattern of $Zr_{0.6}Bi_{0.2}Gd_{0.2}O_{1.8}$ heated in hydrogen atmosphere up 800°C during impedance study	117
<b>Figure 6.11</b>	TGA & DSC curves of $Zr_{0.6}Bi_{0.2}Gd_{0.2}O_{1.8}$ preheated at 120°C	119
<b>Figure 6.12</b>	FT-IR spectra of $Zr_{0.6}Bi_{0.2}Gd_{0.2}O_{1.8}$ preheated at 120 °C	119
<b>Figure 6.13</b>	Dielectric constant of $Zr_{0.6}Bi_{0.2}Gd_{0.2}O_{1.8}$ at different temperatures and frequencies	121
<b>Figure 6.14</b>	Dielectric loss of $Zr_{0.6}Bi_{0.2}Gd_{0.2}O_{1.8}$ at different temperatures and frequencies	121

## LIST OF TABLES

---

Table No.	Table description	Page No.
Table 1.1	Comparison of different types of fuel cells	12
Table 3.1	Structural parameter of Ta and Ge doped $\text{KTaO}_3$	59
Table 3.2	$\text{O}^{2-}$ conductivity ( $\sigma$ ) of $\text{KTa}_{1-x-y}\text{Ti}_x\text{Ge}_y\text{O}_{3-\alpha}$ at different temperatures	63
Table 4.1	Structural parameter of K and Ga doped $\text{BaZrO}_3$	76
Table 4.2	$\text{O}^{2-}$ conductivity ( $\sigma$ ) of $\text{Ba}_{1-x}\text{K}_x\text{Zr}_{1-y}\text{Ga}_y\text{O}_{3-\delta}$ at different temperatures	82
Table 4.3	Activation Energy of $\text{Ba}_{1-x}\text{K}_x\text{Zr}_{1-y}\text{Ga}_y\text{O}_{3-\delta}$	84
Table 5.1	Structural parameter of K and Ga doped $\text{SrTiO}_3$	93
Table 5.2	$\text{O}^{2-}$ conductivity ( $\sigma$ ) of $\text{Sr}_{1-x}\text{K}_x\text{Ta}_{1-y}\text{Ga}_y\text{O}_{3-\delta}$ at different temperatures	97
Table 6.1	Structural parameter of Bi and Gd doped $\text{ZrO}_2$	109
Table 6.2	$\text{O}^{2-}$ conductivity ( $\sigma$ ) of $\text{Zr}_{1-x-y}\text{Bi}_x\text{Gd}_y\text{O}_{2-\delta}$ at different temperatures	113

## **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 <sub>2</sub> O <sub>3</sub> stabilized ZrO <sub>2</sub>
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  $\kappa$  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  $\kappa$  dielectric/ferroelectric  $\text{KTaO}_3$  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  $\kappa$  relaxor dielectricity or polarization in  $\text{KTa}_{0.4}\text{Ti}_{0.3}\text{Ge}_{0.3}\text{O}_{2.7}$ , resulting in high oxide-ion

conductivity at elevated temperatures (Oxide-ion conductivity  $\sigma_o > 10^{-2}$  S/cm,  $T \geq 550^\circ\text{C}$ ). The maxima of the dielectric constant or highest dielectric constant were found at  $\sim 5300$  at applied frequency 20 kHz at  $650^\circ\text{C}$ , and  $T_m$  was varying or decreasing with increasing applied frequency. This linear decrease of  $T_m$  from  $650^\circ\text{C}$  to  $550^\circ\text{C}$  from 20 kHz to 100 kHz of applied frequency confirms the relaxor/leaking nature of high  $\kappa$  dielectric behaviour of  $\text{KTa}_{0.4}\text{Ti}_{0.3}\text{Ge}_{0.3}\text{O}_{2.7}$ . 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  $\kappa$  dielectric in accelerating the motion of oxide-ion vacancies within the percolation limit inside the host crystalline structure. Similarly, doped  $\text{BaZrO}_3$  and  $\text{SrTiO}_3$  are the other perovskites explored in this thesis. To overcome the low ionic conductivity issues of  $\text{BaZrO}_3$  &  $\text{SrTiO}_3$  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  $\text{BaZrO}_3$  and  $\text{SrTiO}_3$  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  $\sim 10^{-2}$  S/cm above  $650^\circ\text{C}$ . The conductivity represented here for  $\text{Ba}_{0.8}\text{K}_{0.2}\text{Zr}_{0.8}\text{Ga}_{0.2}\text{O}_{2.8}$  and  $\text{Sr}_{0.8}\text{K}_{0.2}\text{Ti}_{0.8}\text{Ga}_{0.2}\text{O}_{2.8}$  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  $\text{ZrO}_2$  was stabilized with simultaneous doping of Bi and Gd in the form of  $\text{Zr}_{1-x-y}\text{Bi}_x\text{Gd}_y\text{O}_{2-\delta}$  and was proposed as an oxide-ion conductor to be an electrolyte for IT-SOFC.  $\text{ZrO}_2$  is a key constituent in the perovskite structure, and  $\text{ZrO}_6$  octahedra act as a central point in providing high dielectric and ferroelectric constant in PZT-based perovskite structures. With the incorporation of  $\text{Bi}^{3+}$  and  $\text{Gd}^{3+}$  ions, in conjunction with lone pairs of Bi, the cubic  $\text{Zr}_{1-x-y}\text{Bi}_x\text{Gd}_y\text{O}_{2-\delta}$  phase showed relaxor type high  $\kappa$  dielectric behaviour ( $\epsilon' = 9725$  at  $600^\circ\text{C}$  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,  $T > 500^\circ\text{C}$ ) 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.