PREFACE

Global energy demand is continually rising as a result of ongoing industrial development and population increase. The demand for energy, particularly from liquid fuels, has generated a bottleneck since the early 2000s, resulting in the current energy crisis. The combustion of fossil fuels provides the majority of the energy needed to the world. As a result, the globe is dealing with a variety of issues, including climate change, oil spills, air pollution, acid rain, and so on. Alternatively, wind, solar and hydro-power systems are rapidly growing and gaining popularity all over the world. However, because these renewable energy sources are generally dependent on the weather, their extensive expansion is limited. Wind turbines need wind to turn on their blades, and solar collectors need sunlight to gather heat and generate power. The current cost of renewable energy technology is also far in excess of traditional fossil fuel generation. Furthermore, they are less efficient and non-portable. To address these constraints, ongoing attempts are being made to produce superior, highly efficient, and long-term energy conversion systems. Fuel cell is one of the promising technologies that is expected to meet the majority of these requirements.

A fuel cell is an electrochemical device that converts chemical energy contained in fuels (such as hydrogen, methane, butane, etc.) into electrical energy by exploiting the natural tendency of oxygen and hydrogen to react. High efficiency and fuel adaptability are not the only major advantages of fuel cells, but they are also attractive as they are clean, reliable and almost non-polluting. Furthermore, since there are no moving parts, they are vibration-free. Fuel cells are classified on the basis of the electrolyte they employ. Among them, it has been favoured to choose solid oxide fuel cell (SOFC) because of its durability, portability, and high efficiency. Furthermore, SOFCs are less sensitive to fuel contaminants. SOFC consists of anode, cathode, electrolyte, interconnect and seal. The electrolyte, which is sandwiched between the cathode and anode, is critical to the SOFC's operation. It must have appropriate oxygen-ion conductivity, minimal electrical conductivity, stability in both oxidizing and reducing conditions, and the ability to remain dense and impermeable while the cell is operating. Among all the investigated electrolyte materials, yttria-stabilized zirconia (YSZ) is the most extensively used electrolyte. However, the use of YSZ is restricted due to the electrical conductivity's limiting magnitude and its high operating temperature of over 800 °C. It becomes increasingly important to reduce the operating temperature of the fuel cells down in order to prolong the life span of a cell, the stability of a SOFC, widen the selection of electrodes, interconnect and manifold materials and also to reduce the overall cost of material processing & cell fabrication.

Our present work is focused on the development of the electrolyte materials for intermediate temperature SOFCs (IT-SOFC), with an operating temperature of 500-700 ℃. Among the various available electrolytes, high oxygen diffusivity has been observed for perovskite-based materials. Perovskite structured sodium bismuth titanate ($Na_{0.5}Bi_{0.5}TiO_3$) exhibits high ionic conductivity and transference number. The volatile nature of Bi^{3+} makes NBT a fast ionic conductor. The presence of highly volatile sodium and bismuth makes NBT susceptible to the processing conditions. It exhibits different types of dominant conducting species and nature with slight variation in the concentration and synthesis techniques. Our investigation is focused on the sintering temperature, stoichiometry variation and alteration in the synthesis route of sodium bismuth titanate. Variation from small range hopping to long-range hopping has been suggested with the change in the sintering temperature. Furthermore, a variation from superlinear behaviour to sublinear behaviour with the change in the Na/Bi ratio has been observed.

Non-stoichiometry in the NBT is considered to be one of the significant issues. To overcome this, we synthesized the sample via liquid phase sintering, i.e. Polyol mediated synthesis. It has been observed that the sample synthesized via Polyol mediated synthesis exhibits better conductivity. Also, the systematic study of Mg substituted $Na_{0.50}Bi0._{49}TiO_{3-\delta}$ was the focus of the study. The prepared samples were characterized using XRD, SEM, TGA, Raman, and Impedance spectroscopy.

Besides the NBT, Tri-yttrium gallate was also synthesized and systematically investigated for its application as an electrolyte material for IT-SOFC. The structural, morphological, optical and elemental analyses of these systems have been carried out using the XRD, FESEM, UV-Visible and XPS techniques. The impedance analysis technique has been used to investigate the electrical behaviour and conduction mechanism.

In light of the foregoing, we intend to examine a few classes of innovative electrolyte systems that can operate at intermediate temperatures (500-800 °C) while being substantially less expensive. For this purpose, sodium bismuth titanate and triyttrium gallate has been selected as the electrolyte materials. The structural, microstructural, optical, thermo-dynamical and electrical properties of these materials have been investigated, and the correlation among them is established. This bound volume submitted for the Doctoral degree in IIT BHU comprises seven chapters followed by future work and a list of publications. A brief description is given below:

Chapter 1 deals with the introduction of fuel cells, followed by a brief literature survey. This chapter illustrates the motivation of work, background, and fundamentals of solid oxide fuel cells and the present scenario of electrolyte materials. Moreover, this chapter deals with the various possible conduction mechanism in the investigated systems. The primary goals of the present work are also included in this chapter.

Chapter 2 discusses a detail of the employed experimental instruments and analysis techniques. Solid-state reaction route and polyol mediated synthesis route were adopted to synthesize the samples. This section includes a full description of the instruments used, such as XRD, FESEM, TEM, XPS, DSC, UV-Visible, and Impedance Spectroscopy measurements, as well as significant analysis techniques including Rietveld Refinement and Impedance analysis. The basic physics behind the measurements are also discussed in brief.

Chapter 3 aims to describe the structural properties and ion dynamics of sodium bismuth titanate sample synthesized via solid-state reaction route and sintered at temperature 1000 ℃ to 1150 ℃. Phase formation of NBT was studied by thermal and powder X-ray diffraction techniques. In order to understand the ion dynamics with the sintering temperature, impedance spectra were analyzed. The dc conductivity, hopping frequency and exponent values were extracted from the conductivity spectra analysis. The impedance and modulus spectroscopy along with exponent behaviour suggested short-range hopping for the sample sintered at 1000 ℃ and followed Ghosh scaling instead of Summerfield scaling. While long-range hopping was observed for the samples sintered at 1150 ℃ and it followed both the Summerfield scaling and Ghosh scaling. Moreover, the sample is observed to degrade in reducing atmosphere.

Chapter 4 presents the systematic study on the physical properties of substitutional variation in $Na_{0.5+x}Bi_{0.5-x}TiO_{3-\delta}$ (x = -0.02, -0.01, 0.00, 0.01, 0.02). It has been observed that Bi rich compositions exhibit superlinear frequency-dependent behaviour, and Na rich compositions show sub-linear behaviour. To study the degradation mechanism, $Na_{0.5+x}Bi_{0.5-x}TiO_3$ (x = -0.01, 0.00, 0.01) samples were kept in reducing environment for 48 h. Further, in order to understand the conduction mechanism and the qualitative/quantitative estimation of charge carriers before and after reducing conditions, various models were used.

In **Chapter 5**, bismuth deficient sodium bismuth titanate, i.e. $Na_{0.50}Bi_{0.49}Ti_1O_{3-\delta}$, was synthesized using the Polyol mediate synthesis route. This route of preparation helps to produce fine particles, better surface area and good conductivity at relatively lower processing temperatures as compared to the solid-state reaction route. Mg substituted $Na_{0.5}Bi_{0.49}Ti_1O_{3-\delta}$ samples were found to exhibit higher conductivity as compared to the Bi-deficient samples. A correlation among the phase formation, conduction behaviour and ion diffusion mechanism has also been established for the Mg^{2+} substituted Bi-deficit NBT derived compositions.

Chapter 6 is devoted to the Triyttrium gallate (Y_3GaO_6) based electrolyte systems. Crystal structure, migration path, morphology, thermal properties, conductivity and impedance analysis of all the samples have been discussed employing various characterization techniques. This chapter consists of two sections. In section A, the synthesis of alkaline earth metal substituted Y_3GaO_6 has been studied by the solid-state route and the effect of 2% substitution of Ba, Ca, and Sr on the Y site has been investigated. Section B describes the influence of the higher dopant concentration of Ca on the Y site of Y_3GaO_6. 2% of calcium substituted Y_3GaO_6 has been found to exhibit the highest conductivity.

Chapter 7 concludes the outcomes of the research works of this thesis and also lists the possibilities of future investigations.