



Chapter-7

Conclusion and Future Perspectives



CHAPTER 7: Conclusions and Future Scopes

7.1 Conclusion of the Present Investigation

The research work presented in the thesis has focussed attention on the two classes of electrolyte materials, i.e. Sodium Bismuth Titanate ($\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$) and Triyttrium Gallate (Y_3GaO_6), along with their derivatives, which can be used as solid electrolytes for solid oxide fuel cells (SOFCs). The structural, microstructural, and thermal properties of the systems have been investigated in connection to ionic conductivity, which is one of the essential requirements of electrolytes. Conductivity and impedance spectroscopy techniques were employed to understand the electrical conductivity behaviour. The major conclusion drawn from the entire study carried out during this work are summarized below:

1. Sodium bismuth titanate ($\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$) with different morphology were synthesized via solid-state reaction route by varying the sintering temperature from 1000 °C to 1150 °C. XRD data revealed the formation of polycrystalline rhombohedral phase with the $R3c$ space group. The morphology of the system has a considerable impact on the conductivity. The conductivity spectra were used to deduce the dynamics of ions. The conductivity spectra analysis yielded the dc conductivity, hopping frequency, and exponent values. The impedance and modulus spectroscopy along with exponent behaviour suggested short-range hopping for the sample sintered at 1000 °C and followed Ghosh scaling instead of Summerfield scaling. While long-range hopping was observed for the samples sintered at 1150 °C and it followed both the Summerfield scaling and Ghosh scaling. In addition, the stability of the sample was also checked in the reducing atmosphere.

2. In continuation of the above, ion dynamics of the non-stoichiometric $\text{Na}_{0.5+x}\text{Bi}_{0.5-x}\text{TiO}_{3-\delta}$ ($x = -0.02, -0.01, 0.00, 0.01, 0.02$) samples were investigated. In this context, we synthesized $\text{Na}_{0.5+x}\text{Bi}_{0.5-x}\text{TiO}_3$ with $x = -0.02, -0.01, 0.00, 0.01$ and 0.02 via solid-state reaction route. The XRD confirmed the rhombohedral structure with the $R3c$ space group. The conductivity data isotherms with frequency showed non-linear variation and were well fitted with Jonscher power law. A very small non-stoichiometry doesn't affect the conductivity, but the activation energy varies between 1.4 - 1.8 eV suggesting the variation in charge species. In Bi rich composition, we observed super linear frequency-dependent behaviour and sub-linear behaviour when the Na content increased. To understand the degradation mechanism, $\text{Na}_{0.5+x}\text{Bi}_{0.5-x}\text{TiO}_3$ ($x = -0.01, 0.00, 0.01$) samples were kept in reducing environment for 48 h. After reduction, the conductivity in the Bi rich sample ($x = -0.01$) enhances and with the increase in Na content, conductivity increases in the high-temperature regime and reduces in the low-temperature regime. Furthermore, in all samples, the rise in activation energy of 0.3-0.4 eV is linked to an increase in oxygen vacancies and their coupled electrons.

3. To study the influence of synthesis method on the physical properties of Bi-deficient and Mg^{2+} -doped Sodium Bismuth Titanate. $\text{Na}_{0.5}\text{Bi}_{0.49}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-\delta}$; ($x = 0.00, 0.01, 0.02, 0.03$) samples were synthesized via polyol mediated synthesis route. This preparation route helps to produce fine particles with better surface area and good conductivity at relatively lower processing temperatures as compared to the solid-state reaction route. The Mg^{2+} doping at the Ti^{4+} site improved the sinterability and augmented the grain size. We also explored the influence of Bi-deficient Mg^{2+} -substituted NBT compositions on the electrical conductivity and ion migration behaviours. The conductivity was found to be maximum for $x = 0.02$

composition. At the higher doping concentration of Mg^{2+} ($x > 0.02$), conductivity decreased slightly.

4. In Y_3GaO_6 family system, solid solution of Y_3GaO_6 and 2% of $-\text{Ca}^{2+}$, $-\text{Sr}^{2+}$, & $-\text{Ba}^{2+}$ doped Y_3GaO_6 i.e. $\text{Y}_{(3-0.06)}\text{M}_{0.06}\text{GaO}_{6-\delta}$ ($\text{M} = \text{Ca}^{2+}$, Sr^{2+} & Ba^{2+}) were prepared via conventional solid-state reaction route. X-ray diffractograms of all the compositions confirmed the formation of an orthorhombic structure having the $Cmc2_1$ space group. It was observed that the aliovalent doping of Ca^{2+} , Sr^{2+} and Ba^{2+} enhanced the conductivity by increasing the oxygen vacancy concentration. However, among all the studied dopants, 2% of Ca^{2+} -doped Y_3GaO_6 was found to be more effective in increasing the ionic conductivity as ionic radii mismatch is minimum for $\text{Y}^{3+}/\text{Ca}^{2+}$. This is accounted to the optimum dopant size mismatch with the host ion as it produces minimum strain in the crystal lattice. Total electrical conductivity measurement as a function of oxygen partial pressure suggests dominating oxide ion conduction in a wide range of oxygen partial pressure ($\sim 10^{-20} - 10^{-4}$ atm). The oxygen ion transport is attributed to the presence of oxygen vacancies that arise from doping and conducting oxide ion layers of one, two- or three-dimensional channels within the crystal structure.

7.2 Outlook for Future Perspective

The intriguing properties of electrolyte materials for SOFC depend on their processing route, dopants concentrations and microstructures. These parameters must be optimized in order to get good ionic conductivity and improved material performance. Processing variables like sintering temperature, environment utilized during sintering, processing routes, and the amount of second phase infiltration all affect the microstructure. Therefore, a thorough investigation of the impact of these processing factors on the structural, microstructural,

thermal, and electrical properties of the compositions under investigation is necessary. As a result, the structure-property relationship gives new insight into the role of oxygen ion conductivity in suggested electrolyte systems with A and B site doping.

Some of the following points may be noted for future prospects in this area:

- The conductivity behaviour of all the investigated compositions may be investigated at various partial pressures of oxygen to know the pressure range in which conductivity is purely ionic.
- The transference number may be examined as one of the most critical criteria in estimating the conductivity of electrolyte samples.
- Thin films and tapes may be fabricated using various techniques to optimize the ionic conductivity of the electrolyte systems.
- Adoption of composite and bi-layered electrolytes may be an available approach to enhance the performance of SOFC.
- The thermal and chemical stability of materials may be tested for their application as electrolyte materials.
- The performance of the optimized solid electrolytes by sandwiching them between compatible anodes and cathodes may be checked and verified for a unit cell.
- Theoretical investigation of the ionic conductivity may be carried out using DFT calculations because it may be utilized to investigate how dopant types and concentrations affect ionic conduction and comprehend the principles of diffusion in doped electrolyte systems.