

Chapter-7: Conclusion and Future Scope

7.1 Conclusion of the Present Investigation

Overall thesis work, It has been concluded that lanthanum aluminate is a cost effective and high oxide ion conducting electrolyte material for solid oxide fuel cell. We have studied structural, microstructural and thermal properties of the investigated system and established a correlation between the critical angle and electrical conductivity. We have also concluded that conduction is due to the vibration of phonon which force the zone boundary transition (ZBT). Now, on the basis of the results summary of the present work is as follows:

1. The investigated system LaAlO_3 (LAO) has been prepared successfully by citrate nitrate auto combustion route. The Thermal analysis and powder X-ray diffraction pattern showed the single phase formation of the system at 700 °C having rhombohedral perovskite structure with space group R-3c. SEM observation clearly shows that the grains have rhombohedral shape that is justified by TEM also. The crystallite size and grain/particle size is found to be ~47 nm and ~74 μm , respectively. HRTEM analysis exhibits the interatomic spacing is 0.27 nm corresponds to (110) plane of rhombohedral lattice of the systems. SAED analysis also confirms the well polycrystalline rhombohedral structure. The XPS spectra confirm that the constituents are present in their characteristic chemical state in the system. In the studied system, the charge carriers are temperature independent and the conductivity is mainly depending on the mobility of the charge carriers. Oxide ions are mainly involved in the conduction process as the charge carriers. The dc and ac conductions are correlated in the system. The scaling of the conductivity spectra follows the Ghosh scaling. This indicates that the hopping frequency is a suitable scaling parameter for the system.

2. A systematic study on structural properties of Ba modified $\text{La}_{0.9}\text{Sr}_{0.1}\text{Al}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ and its correlation with conductivity has been carried out. It is observed that value of conductivity can be better correlated with critical triangle angle rather than length of its sides. Consequently, A site substitution with and without B- site substitution, effectively controls the ionic conductivity. However, aliovalent substitution at A site with larger ionic radii decreases the oxide ionic conductivity and it may increase with smaller ionic radii.

It is concluded that B1 ($\text{La}_{0.89}\text{Sr}_{0.1}\text{Ba}_{0.01}\text{Al}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$) tape has been prepared by the tape casting method using the Doctor's blade technique has lower conductivity than that of the pellet of the same electrolyte system. The XRD pattern shows a rhombohedral perovskite structure with the shifting of peaks corresponding to 2θ value at $\sim 22^\circ$ or 32° . The activation energy extracted from Nyquist plots, Jonscher power law fitting and using relaxation time are in good agreement. The values of exponent factor (K) lie in the range of 0.7 - 0.2, which reveals the formation of ionic charge carriers and EDAX measurements confirm the higher oxygen content in tape casted samples. The low conductivity of the tape could be because of less number of oxygen vacancies and accumulation of Ba impurity at the grain boundaries.

3. In Sm incorporated $\text{La}_{0.9}\text{Sr}_{0.1}\text{Al}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$, it is found that with small ionic radii and high valence has decreased the ionic conductivity. On the basis of transference number (T_f), it is concluded that Sm substituted $\text{La}_{0.9}\text{Sr}_{0.1}\text{Al}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ is II type ionic conductor. The conductivity of the investigated systems is in good correlation with critical triangle angle B-A-B (α) and A-B-B (β) as also seen in earlier systems. Also, transition of investigated system from rhombohedral (R-3c) to pseudo cubic (R-3c) is due to zone boundary transition (ZBT) through R_{25} soft phonon mode at $\sim 500^\circ\text{C}$. This

transition has been correlated with the octahedral tilting, which is minimum at ~ 500 °C. Also, critical triangle angles are found to possess minima at this temperature concluding that this transition is not a phase transition rather it is a phonon mode transition. Hence, before and after 500 °C, it is rhombohedral in structure; however this particular transition is viable for the electrolyte materials, due to enhancement in conductivity.

4. To study the oxide ion conduction pathways differential impedance analysis on Ag/M/Ag with Pt/M/Pt where $M = \{La_{0.9-x}(A)_x\}Sr_{0.1}Al_{0.9}Mg_{0.1}O_{3-\delta}$ ($A = Ba, Sm$) for $x=0.00$ and 0.03 has been done. The ionic conductivity of S3 is smaller as compared to B0 and B3. According to the transference number, B0 is highly ionic with high ionic conductivity in spite of the fact that B3 has higher value of total conductivity. In our system, zone boundary transition around which there is a transition from small to large polaron or vice versa is facilitated through Pt electrodes. It can be concluded that the Pt paste supports the motion of oxygen ions by not disturbing the inherent oxide ion channels of the electrolyte material whereas Ag doesn't support the oxide ion channels as the value of fractal exponent indicates the hindrance created by the host ions.

1. The density of all the samples is about 95 % of theoretical density after sintering at 1300 °C.
2. The value of activation energy obtained shows that the conduction process for all samples is mainly due to diffusion of O^{2-} ions through oxygen vacancies.

7.2 New Directions and Future Perspectives

The intriguing properties of electrolyte materials like microstructure, density, thermal and electrical compatibility for solid oxide fuel cells (SOFCs) depend on their synthesis route, dopants concentrations and microstructures. In this context, to achieve good conductivity and better performance of the materials, these parameters must be optimized. The microstructure is quite sensitive to the processing parameters such as

sintering temperature, atmosphere used during sintering, processing routes and also the amount of extra phase infiltration. So a detailed study on the effect of these processing parameters on the structural, microstructural, thermal and electrical properties of the investigated compositions is required. Therefore, the structure-property correlation reveals the deep insights to understand the influence of oxygen ion conductivity with A and B site doping of proposed perovskite electrolyte systems.

One important direction is to exploit the novel exotic electrolyte system from a simple, robust and cost effective chemical method in order to transcend some of the difficulties facing materials development for low and intermediate temperature SOFCs. Although vigorous efforts are made to experimentally characterize ionic diffusion and to develop optimal electrolytes through structure-property correlation, experimental studies do not lend to an understanding of the mechanism of ionic conduction at the atomic level. Another important new direction is to develop a predictive (density functional theory (DFT)) computational framework by carefully designed experiments, for the rational design of better electrolyte materials and structures for a new generation of SOFCs. This understanding is important in order to develop better ionic conductors. Therefore, the thrust of area is to develop a fundamental understanding of oxygen vacancy migration at the atomic level for perovskite based and other electrolyte systems.

Therefore the keeping above view the following points are considered for the future prospect in these regimes:

1. Some of the novel and exotic electrolyte system should be developed which can have optimized ionic conductivity and may be considered in perspective of chemical and thermal stability and most importantly their operation at low or intermediate temperature range.

2. The conductivity behavior of the sample at different partial pressure of oxygen should be studied to know the pressure range in which the conductivity is purely ionic.
3. The transference number is one of the important factors to predict the nature of the conductivity of electrolyte samples.
4. A fine and excellent quality of tape should be fabricated using tape casting method for optimized ionic conductivity of electrolyte systems by proper optimization of slip rheology using appropriated wt% of dispersant, solvent, binder, plasticizer and de-foamer.
5. The performance of the optimized electrolyte systems may be checked their compatible with anodes and cathodes.
6. Measurement of thermal expansion coefficient will be useful to study the compatibility of these electrolytes with the other component of cells.
7. Tape of bilayer composite electrolyte film should be formed to enhance the ionic conductivity as well as reduce the operating temperature that can be feasible for low and intermediate temperature SOFCs.
8. A theoretical investigation of the ionic conductivity is important that should be carried out using DFT calculations because it can be used to explore how dopant types and dopant concentrations influence the ionic conduction and to understand the mechanisms of diffusion in doped electrolyte systems.

