Preface

This thesis represents a culmination of work and better learning that has taken place in the last couple of years. Nowadays energy markets are dominated by a substantial increase in energy demand due to the strong economic growth in the developing countries in all over the world. Limited fossil fuel reserves and continuous ecological degradation compelled governments and industries all around the world to look for renewable energy sources and technologies for power production. Alternate energy resources are considered a long-term solution to the world's future energy demands, as they are environment-friendly and independent of our declining limited natural resources. Several forms of alternate energy technologies are presently used around the world for small-scale electricity production. Due to limitations of these alternative energy sources it is better to look for sufficiently develop renewable energy resources. Among the available renewable energy sources & energy conversion devices, a fuel cell is an emerging technology for efficient and clean power generation.

A fuel cell is an electrochemical device that converts chemical energy into electrical energy by exploiting the natural tendency of oxygen and hydrogen to react. Fuel cells are classified on the basis of electrolyte they employed. It has been desired to choose solid oxide fuel cell (SOFC) due to its durability, stability, reliability, high efficiency and solid electrolyte. There are mainly three components of SOFC: Anode, Cathode and Electrolyte. The recent work has been focused on the development of cost effective electrolyte material of SOFC. The electrolyte must have sufficient oxygen ion conductivity and also chemical stablility in a large oxygen

partial pressure gradient from highly reducing (anode) to oxidizing conditions (cathode). It should be thin also to minimize resistive losses in the cell.

Among the other electrolytes like YSZ, $LaGaO_3$, Ceria based electrolytes, etc. lanthanum aluminate ($LaAlO_3$) has a low operating temperature, no leakage current, not expensive, high mechanical strength and stablility in both the thermal and chemical conditions.

In order to synthesize lanthanum aluminate based electrolyte materials, it has been opted citrate-nitrate auto combustion synthesis technique to get nano range particles and tape casting technique to get thin electrolyte. Some instruments like: XRD, FESEM, TEM, XPS and FTIR have been used for characterization of the electrolyte system. The differential impedance analysis techniques conductivity spectroscopic techniques have been used to understand the conduction mechanism of investigated system lanthanum aluminate.

In order to enhance conductivity it has been proposed lanthanum aluminate ($LaAlO_3$), co-doping of Sr and Mg on La-site and Al-site of $LaAlO_3$ and double doped system on A-site to enhance the ionic conductivity and found that an alio-valent double substitution with Ba can enhance the ionic conductivity than that of an iso-valent substitution with Sm.

Also, I have prepared thin tape one of the investigated systems with the help of Doctor's blade instrument and found that proper optimization of all the aspects are necessary in order to get the tape.

In this thesis, it has been proposed the conduction pathways for oxide ions by using different electrode like silver (Ag) and platinum (Pt) and study their effects on conduction mechanism, also.

The most interesting facts in present study is that there occurs a transition from rhombohedral (R-3c) to pseudo cubic (R-3c) at nearly 500 °C for investigating system. This type of transition is known as zone boundary transition (ZBT) and occurs due to R_{25} soft phonon mode at ~500 °C. This transition has been correlated with the octahedral tilting, as it is minimum at ~ 500 °C. Also, critical triangle angles are found to possess minima at this temperature concluding this transition is not a phase transition rather it is a phonon mode transition. Hence, before and after 500^{o}C it is rhombohedral in structure, but this transition is useful for the electrolyte materials as this has increased the conductivity.

The objective of the whole thesis is divided into seven chapters and a brief description is given below:

The **first chapter** of this thesis illustrates motivation of the work, backgrounds of solid oxide fuel cell (SOFC), basic of the electrolytes for solid oxide fuel cell (SOFC), present scenario of electrolytes, lanthanum aluminate based electrolyte materials and literature survey.

The **second chapter** represents a detailed of the employed experimental instruments and analysis techniques. Citrate-nitrate auto combustion method and tape casting technique were used to synthesize the investigated systems. A detailed description of the employed instruments like XRD, SEM, TEM, XPS etc. and some analysis techniques like Rietveld refinement, differential impedance analysis have mentioned in this section.

The **third chapter** describes structural properties and ion dynamic of base material $LaAlO_3$. Phase formation of $LaAlO_3$ was studied by thermal and powder X-ray diffraction techniques. Morphology and elemental confirmation was studied by Optical Microscope and XPS, respectively. The electrical measurement of the

investigated system was measured using Wayne Kerr 6500P LCR meter in the frequency range 20 Hz to 1 MHz and in the temperature range (300-750) ºC. The conductivity data were analysed in terms of Jonscher power law fitting. The activation energy implies that the conductivity is mainly dependent on the mobility of ionic charge carriers. Ghosh scaling shows, only single charge carriers play a role in the conduction. Modulus spectra were used to support the given information about conduction mechanism.

The **fourth chapter** describes a systematic study of structural properties of Ba-substituted $La_{0.1}Sr_{0.1}Al_{0.9}Mg_{0.1}O_{3-\delta}$ (LSAM) and its correlation with conductivity. Electrical conductivity was found to be in correlation with new structural parameter of the critical triangle. Activation energy was correlated with the area of the critical triangle. It was found that an alio-valent double substitution on A-site having larger ionic radii can increase the ionic conductivity. In continuation of **chapter four**, a novel approach to maintain the thickness of the electrolyte. It was prepared a thin tape of $(La_{0.89}\ Ba_{0.01})\ Sr_{0.1}Al_{0.9}Mg_{0.1}O_{3-\delta}$ using Doctor's blade techniques. A comparative study of the tape casted specimen and pellet was done.

The **fifth chapter** present effects of an iso-valent A-site double substitution having lower ionic radii on conductivity. It was investigated that Sm-substituted $La_{0.1}Sr_{0.1}Al_{0.9}Mg_{0.1}O_{3-\delta}$ (LSAM) decrease the ionic conductivity. A similar analysis was done in chapter five as analyzed in chapter four. Also, it was discussed the conduction mechanism of phase transition in terms of zone boundary transition (ZBT) and R_{25} phonon mode.

In **sixth chapter,** Differential impedance analysis has been applied to study the effect of the electrode/electrolyte interface on the conduction behaviour in solid oxide fuel cells (SOFC). For this, a comparative investigation of Ag/M/Ag with Pt/M/Pt

where M = $(La_{0.9-x}(A)_x)$ $Sr_{0.1}$ $Al_{0.9}$ $Mg_{0.1}$ $O_{3-\delta}$ having A = Ba, Sm for x=0.00 and 0.03 has been done. 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.

Finally, **seventh chapter** describes the summary of the present thesis and future research work.