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 as a proton conductor. The electrolyte must have sufficient oxygen ion conductivity and also chemical stability 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. Strontium Cerate ($SrCeO_3$) has a low operating temperature, no leakage current, not expensive, high mechanical strength and stability in both the thermal and chemical conditions.

$SrCeO_3$ is a perovskite and general formula of perovskite is ABO_3 where valences of A and B cations +1,+2,+3 and +3,+4,+5 respectively. The ideal perovskite structure has a cubic unit cell, space group Pm3m that and contains one formula unit but SrCeO3 has orthorhombic crystal structure with space group Pnma. It is known that the probabilities of substitutions at A or B site in perovskite oxides ABO_3 depends on the valence state and ionic radii corresponding to the coordination number (CN) of the dopant ion and the substituted site-ion. In perovskite oxide $SrCeO_3$, the coordination number of Sr is 12 while of Ce is 6. Due to distortion, perovskite structure have different structure depends upon the value of the tolerance factor (t) and as well to analyse the stability of the structure of perovskite oxides Goldschmidt suggested a parameter known as Tolerance factor (t) is defined as:

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$

In this work we have synthesized $SrCeO_3$ and other new compounds by selecting suitable acceptor dopants for Ce^{4+} site. At Ce^{4+} site three dopants Na^+ (monovalent), La^{3+} (hetrovalent acceptor), Gd^{3+} (hetrovalent, acceptor) have been incorporated. The effect of incorporation of these dopants on the crystal structure, microstructure, electrical properties of $SrCeO_3$ have been investigated. To the best of our knowledge, no report is available on the substituted materials in the literature so far. The results of these investigations are described in chapters 3-6 of the thesis. In this work following systems have been synthesized by solid state ceramic route:

(i) Pure $SrCeO_3$.

(ii) Na^+ doped at Ce^{4+} site $SrCe_{1-x}Na_xO_3$ (x=0.0,0.02,0.04,0.6 and 0.10)

(iii) Gd^{3+} doped at Ce^{4+} site $SrCe_{1-x}Gd_xO_3$ (x=0.0,0.02,0.04,0.6 and 0.10)

(iv) La^{3+} doped at Ce^{4+} site $SrCe_{1-x}LaO_3$ (x=0.0,0.02,0.04,0.6 and 0.10)

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), Strontium Cerate based electrolyte materials as a proton conductor and literature survey.

The **second chapter** represents a detailed of the employed experimental instruments and analysis techniques. Solid state technique were used to synthesize the investigated systems. A detailed description of the employed instruments like Thermogravimetri and Differential scanning calorimetry (TGA/DSC), power X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman, X-ray photoelectron spectroscopy (XPS) etc. and some analysis techniques like Rietveld refinement, differential impedance analysis have mentioned in this section.

The **third chapter** deals with Strontium cerate ($SrCeO_3$) based proton conducting system. Crystal structure, ion dynamic, electrical conductivity, impedance analysis and PL spectroscopy of pure $SrCeO_3$ prepared by solid state method have been discussed.

The **fourth chapter** results on synthesis and characterization of Na^+ doped at Ce^{4+} system, $SrCe_{1-x}Na_xO_3$ (with x = 0.00, 0.02, 0.04, 0.06, 0.10) have been discussed. All the synthesized compositions have orthorhombic structure and Pmna space group. The scanning electron micrograph (SEM) of calcined powder of a representative sample shows that particles are agglomerated and irregular in shape with average size 1.8 μm. AC conductivity of the sintered ceramics have been studied in the temperature range 50 to 600°C and frequency range 20 Hz-2MHz.

The **fifth chapter** describes the results on structural and electrical characterization of system $SrCe_{1-x}Gd_xO_3$ (with x=0.00, 0.02, 0.04, 0.06 and 0.10). All the synthesized samples have orthorhombic crystal structure and space group Pmna like undoped $SrCeO_3$. Further, single phase formation of the solid solutions is reconfirmed by their FTIR and Raman spectrum analysis. The AC conductivity of sintered samples measured as a function of frequency and temperature. The highest electrical conductivity is obtained for sample with x=0.02 which is of the order of 10^{-3} Scm^{-1}. The presence of defects and oxygen vacancies (V_O^x) are probed by XPS technique.

The **sixth chapter** concludes the brief overview and results & discussions on La^{3+} doped strontium cerate electrolyte system as proton conductor, synthesized by auto combustion technique. The structural, optical properties, electrical conductivity and complex plane impedance analysis on this system have been incorporated.

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