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## PREFACE

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The need for energy is increasing daily as a result of urbanization and industrialization, whereas conventional fossil resources like oil, coal, natural gas, etc., are quickly running out. These fossil fuels currently serve as our main source of fuel for meeting our energy requirements. However, there is serious cause for concern over the supply of fossil fuels in the coming years. The use of conventional energy sources is hampered by the burning of fossil fuels releasing harmful gases posing number of environmental risks. Global warming is possible by these negative environmental repercussions. The growing awareness of the energy crisis and greenhouse gas emissions has prompted a search for alternative routes. To identify an alternate potential for alternative pathways, the research is divided into two parts, first of which is focused on renewable and ecofriendly sources and second on electrochemical devices such as fuel cells.

Electrochemical devices for energy storage will play a crucial role in a world dependent on energy to address the fast depletion of fossil resources. Electrochemical devices either produce electricity from a chemical reaction (such as a battery) or use electrical energy to initiate a chemical reaction (like a catalyst). Among the many available electrochemical devices, fuel cells are the most efficient and offer a variety of advantages for mobile and stationary power generation, such as large-scale centralized power generation as well as power generation in individual homes and enterprises, etc.

There are currently a variety of fuel cell types available for purchase. Electrolyte substance is typically used to classify fuel cells. Their power outputs, operating temperatures, electrical efficiency, and common applications differ. Solid oxide fuel cells (SOFCs) are one of the cleanest and most efficient methods for directly converting a range of fuels to electricity. SOFCs powered by natural gas are ideally suited for distributed power generation, for instance. However, the commercialization of SOFC technologies is contingent on the development of new materials that can both cut costs and improve performance and durability.

One of the crucial hurdles to achieve high- performance SOFC systems is the electrolyte. Electrolyte sandwiched between anode and cathode is the central component of SOFCs which play a crucial role in the current conduction. In the cell, oxygen molecule has been converted into oxygen ions that must migrate through the electrolyte to the fuel side. It is a key component of SOFCs. For the migration of oxygen ions, electrolyte must possess a high ionic conductivity and no electrical conductivity. It must be fully dense to prevent short-circuiting of reacting gases throughout it. It should be thin also to minimize resistive loss in the cell. As with the other materials, it must be chemically, thermally, and structurally stable over a wide range of temperature.

Due to its pure ion conducting properties over a large range of oxygen partial pressures and ease of manufacture of high-density ceramics, yttria stabilized zirconia (YSZ) is widely employed as the solid electrolyte in most SOFCs. Apart from YSZ, there are other types of oxide ion conducting materials, including fluorite (doped  $\text{CeO}_2$  and  $\text{Bi}_2\text{O}_3$ ), Perovskite ( $\text{LaGaO}_3$ ,

LaAlO<sub>3</sub>), Brownmillerite (Ba<sub>2</sub>Ln<sub>2</sub>O<sub>3</sub>), Aurivillius (BIMEVOX), Pyrochlore (Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>), LAMOX and Apatite-type oxide. Researchers are intrigued by the high oxide ionic conductivity of apatite-type lanthanum silicate oxide materials, which is equivalent to typical oxide ion conductors such as yttria stabilized zirconia. With the general formula  $La_{9.33+x}Si_6O_{26+1.5x}$  ( $x = 0-0.67$ ), lanthanum silicate apatite (LSA) exhibits a high conductivity in the intermediate temperature range and a high oxygen transference number over a broad range of oxygen partial pressures. The apatite-type phases  $La_{10}Si_6O_{27}$  have generated a lot of interest as possible electrolytes for solid oxide fuel cells (SOFCs). Low activation energy for ionic conduction and relative stability characterizes apatite. Rare earth cations are present in the apatite crystal's seventh and ninth coordinated cavities. Apatite-type lanthanum silicates are composed of lone tetrahedral SiO<sub>4</sub> units, which have a space group P6<sub>3</sub>/m in their hexagonal crystal structure. The remaining oxygen ions are dispersed via one-dimensional channels throughout the structure. Strong conduction has been seen as a result of a process in which interstitial oxygen ions migrate through cavities positioned along the c-axis between La channels and isolated SiO<sub>4</sub> tetrahedra. According to neutron powder diffraction atomistic computer modeling and HRTEM observation, which differ from other oxide-ion conductors, the oxygen ion journey in LSA happens by an interstitial-type transport mechanism. The conductivity of LSO rises with La concentration in  $La_{9.33+x}Si_6O_{26+1.5x}$  because additional oxygen ions are injected into the interstitial location of the lattice. Below 650°C,  $La_{9.92}Si_6O_{26.88}$  gives a better conductivity than YSZ. As a result, numerous researchers have explored the all-possible mechanism of conduction in apatite bases ion conductors

The apatite based FOICs (discovered by Nakayama in 1995) showed high ionic conductivity like perovskite based FOICs in low temperature regime (LTR). Among these FOICs, due to its anisotropic ion conduction ( $\sigma_c^{\parallel}/\sigma_c^{\perp} > 10$ ), lanthanum silicate oxyapatite i.e.,  $La_{10-\alpha}^{3+}(SiO_4)_6^{4-}O_{2+\delta}^-$  (LSO) is most interesting and attracted the researcher. Various experiments and theoretical studies predict that  $O_{int}$  (interstitial Oxygen) promotes cooperative movements between the O4 ion and excess oxygen is introduced as interstitial charge carriers to maintain electrical neutrality with La ions. There are 4 channels proposed for the conduction. Channels no. 1 and 2 are formed by the oxygen vacancies in between La(4f)-O4, channel no. 3 is nearest to the Si vacancy site and channel no. 4 is linked to the formation of oxygen Frenkel defects. Thus, there is scope of conductivity enhancement in polycrystalline LSO. In polycrystalline sample, grain alignment and doping are the two common methods to get the desired properties in the sample, the same has been employed by various research groups in the last few years. Grain alignment and c-axis alignment is done by various methods such as sol-gel and arc melting, respectively. Various doping such as Al, Mg at B-site and Alkaline earth and rare earth substitutions at A-site have been done in order to get conductivities in the range of 1 S/cm but unfortunately, conductivity is achieved in the range of 10-50 mS/cm. Though the two kind of conduction mechanism, namely, push pull and interstitial are well described for the oxyapatite but its dynamics is still scarce at large. Thus, in the present thesis, we are investigating the alteration in the structural and dynamics disorder with various substitution in the LSO.

In order to understand the conductivity of LSO and its composition as an

electrolyte material we synthesized the lanthanum silicate  $\text{La}_{9.67}\text{Si}_6\text{O}_{26.5}$

The present thesis is divided into seven chapters and a brief description is given below:

**Chapter 1** It begins with a brief introduction to fuel cells and continues with an exhaustive review of the relevant literature. This chapter discusses the background and fundamentals of fuel cells, the essential requirements of fuel cell components, the mechanism and kinetics for the components of the SOFC, the materials selection for electrolyte, and the conduction mechanism of the apatite-based electrolyte materials. It also explains the motivation behind the research work that was done. This chapter contains the primary purpose of the study that is being presented here as well.

**Chapter 2** discusses various experimental techniques used for the present investigations. It represents the details of implemented experimental instruments, analysis techniques and solid-state synthesis route adopted to synthesize the samples. A detailed description of employed instruments such as TGA, DSC, XRD, SEM, XPS, and impedance measurements, etc. along with the important analysis techniques like Rietveld Refinement analysis has also been discussed in this section. We also discussed the migration analysis using softBV application.

**Chapter 3** The apatite type single phase  $\text{La}_{9.67}\text{Si}_6\text{O}_{26.5}$  samples was synthesized by solid state reaction route method. XRD patterns confirms the formation of pure crystalline apatite-type single phase with hexagonal structure having space group  $P6_3/m$ . Rietveld refinement of the XRD data reveals the crystallographic

information of the system. Thermal study shows the formation of well crystallized lanthanum silicate apatite sample. SEM characterization reveals that particles are highly dense but agglomerated and average grain size was found 2-5  $\mu\text{m}$ . Conductivity spectroscopic technique shows that conduction is due to mainly mobile oxide ions. Dimensionality has been calculated based on Jonscher's power law exponent factor and it was found the predominantly one-dimensional migration of oxide ion through the interstitials. This was further confirmed by the bond balance energy landscape analysis of the system. Sample (sintered at high temperature of 1400  $^{\circ}\text{C}$ ) shows low activation energy ( $E_a = 0.69 \text{ eV}$ ) with the very high dc conductivity of about  $1.4 \times 10^{-2} \text{ Sm}^{-1}$ , measured at 700  $^{\circ}\text{C}$ . This indicates that this system can be used as solid electrolyte for SOFC applications.

In **Chapter 4, We** discussed the influence of the ionic radii on the conduction mechanism in lanthanum silicate oxyapatite, with the alteration of La site with different ionic radii to form  $(\text{La}_{1-x}\text{A}_x)_{9.67}(\text{SiO}_4)_6\text{O}_{2+\delta}$  ( $x = 0.0, 0.05, 0.10, 0.15$ ) where  $\text{A} = \text{Ca}$  and  $\text{Ba}$ . The ionic radii of substituents will alter the average area of critical triangle (saddle point). The structural, microstructural, electronic and conductivity studies was performed using XRD, SEM, XPS and impedance measurement. With ionic radii variation, ion mobility volume has risen to nearly 3 times in Ca substituted sample than Ba substituted sample. We have obtained La deficient Ca substituted samples and O deficient Ba substituted samples. Further, XPS, TGA and Rietveld refinement confirm the formation of La and O deficient Ca and Ba substituted samples, respectively.

In **Chapter 5**, A series of apatite-based lanthanum silicate  $(La_{1-x}A_x)_{9.67}(SiO_4)_6O_{2+\delta}$  ( $x = 0.0, 0.05, 0.10, 0.15$ ) with Ca doped was synthesized using the high temperature solid-state route and their conductivity probed. Powder X-ray diffraction was used to determine the phase formation and structure of the prepared oxides. SEM analyses confirm the morphology of prepared catalysts. This series of apatite-based oxide materials exhibit higher oxide ion conductivity with lower activation energy and the activation energy increases with La vacancies. We have obtained La deficient and O rich samples with Ca substitution. The conductivity, due to connected grain growth increased for  $x = 0.1$ .

**Chapter 6** concludes the outcomes of the research works of this thesis and propose the future scope of the present investigations.