Chapter 1
Introduction

Solid ionic conductors have always contributed a fascinating interdisciplinary field of study ever since their discovery by Faraday over 200 years ago. More recently the pace of research has been rapidly driven by the requirements for new clean energy sources, sensors and high energy density batteries. Considering the relevance of ionic conductors, its properties and applications are discussed in this chapter. The ionic conductors currently under development for application in solid oxide fuel cells are also reviewed in this chapter. The study and application of these fascinating materials provide fertile ground for research in future.
1.1 Solid electrolytes: general characteristics

Solid ionic conductors have high electrical conductivity well below their melting points as a result of ionic motion and they can be used as solid electrolytes in several applications. Solid electrolytes having high ionic conductivity at room temperature are termed as fast ionic conductors or super ionic conductors [1]. The general characteristics of solid electrolytes are given below:

1. A large number of the ions of one species should be mobile. This requires a large number of empty sites, either vacancies or accessible interstitial sites.
2. The empty and occupied sites should have similar potential energies with low activation energy barrier for jumping between neighboring sites. High activation energy decreases carrier mobility, very stable site lead to carrier localization.
3. The structure should have a solid framework, preferably 3D, permeated by open channels. The migrating ion in the lattice should be mobile.
4. The framework ions should be highly polarizable. Such ions can deform to stabilize transition state geometries of the migrating ion through covalent interactions [2].

1.2 Ionic transport in solid electrolytes

High ionic conductivity with low activation energy in solid electrolytes relative to normal defective solids requires the presence of a large concentration of charge carriers with high mobility. Some solid electrolytes such as α-AgI are characterized by a high degree of intrinsic disorder in the Ag⁺ ion sub lattice, resulting in a random distribution of Ag⁺ ions over an excess number of equivalent sites, leading to ion hopping between crystallographic sites. Another feature of such ionic crystals is the increase in high entropy of a solid-solid phase transition which makes the material a good conducting phase [3].
In some other solid electrolytes, the intrinsic disorder is created as a consequence of forming a metastable phase, e.g. by rapid solidification of a melt to form a glass. In another group of materials, fast ionic conductivity is introduced extrinsically by doping, e.g. addition of aliovalent Y$_2$O$_3$ to ZrO$_2$ leads to the formation of oxygen vacancies which makes Y$^{3+}$ doped ZrO$_2$ a good ionic conductor.

In order for an ion to move easily in a solid, a special array of atom or ions in the material is necessary. This array requires either several large clearances for the mobile ions or a number of lattice defects through which a certain ion can move. The former structure can be constructed by large ions as host constituents and the latter can be induced by the introduction of some dopants. In both the cases, rare earths play an important role and hence rare earth elements are vital constituents of many prominent solid electrolyte systems.

Rare earth ions as the constituent of solid electrolytes have the following features:

1. they behave as stable trivalent cations with large ionic radii
2. they provide different sizes of trivalent ions
3. their electronegativity is small and they function as a constituent with strong ionicity
4. they provide a variety of ions which are stable under given conditions and
5. they exhibit characteristics expected of 4f electrons [4].

1.2.1 Ionic conduction

Any charged particle that can be accelerated by an electric field can participate in conduction. The ionic mobility is extremely small compared with electronic mobility and ions can conduct only by means of diffusion through the lattice. Such diffusion requires the existence of vacancies or interstitials. The mobility of the carrier is related to the tracer diffusion coefficient $D_T$, provided that the tracer and defect move by the same mechanism. Then, ionic conductivity

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\[ \sigma_i = n_i Z_i q i \mu_i = D_i Z_i^2 q^2 n_i / f \kappa T \]  

(1.1)

where \( \sigma_i \) – intrinsic conductivity
\( n_i \) – concentration of charge carrier
\( q \) - magnitude of the electronic charge
\( Z_i \) – the number of units of charge carried by defect
\( f \) – correlation factor (=1 for interstitial diffusion, <1 for vacancy diffusion)
\( \kappa \) - Boltzman’s constant and
\( T \) - absolute temperature.

Activation energy of approximately 1-5eV is required to create an interstitial – vacancy pair and energy of equivalent magnitude to move the vacancy or interstitial ion through the material. The total conductivity is given by,

\[ \sigma = \sigma_0 \exp (-E_a / \kappa T) \]  

(1.2)

where \( \sigma_0 \) - a pre exponential factor
\( E_a \) - apparent activation of conduction process
\( \kappa \) - Boltzman’s constant and
\( T \) - absolute temperature.

Thus a graph of log ionic conductivity versus reciprocal temperature can be plotted and the graph gives a straight line. The activation energy can be calculated using the above equation and slope calculated from the graph.

1.3 Types of ionic conductors

Recent developments in the field of ionic conductors increased the number of cation and anion conductors. Cation conductors consist of alkali, copper, silver, proton and other ion conductors; anion conductors are almost exclusively composed of fluorine.
and oxygen ion conductors [5]. Brief description of various ion conductors is given below.

1.3.1 Lithium ion conductors

Lithium ion conductors found application as solid electrolyte membranes in high energy density batteries. Besides ordinary Li$^+$ conductors involving Li$_4$ZrO$_4$, Li$_2$O and Li$_5$AlO$_4$, several materials have been reported to exhibit a high ionic conductivity. The conductivity of Li$^+$ conductors depends on temperature. The highest conductivity of $3 \times 10^{-4}$ (Ω.cm)$^{-1}$ was reported for the layer structured Li$_3$N [6]. Major disadvantages of this system include, its low deposition voltage and formation of electrically short circuiting dentrites.

To overcome these problems, ternary compounds based on Li$_3$N have been developed, which include the system Li$_3$N-LiCl. But the presence of hydrogen in this system affects the vacancy concentration and the activation energy for conduction.Li$_{1.9}$Cd$_{1.05}$Cl$_4$ with the spinel structure was found to exhibit a high ionic conductivity [7]. Another class of Li$^+$ conductors is the solid solutions based on Li$_4$SiO$_4$ or $\gamma$Li$_3$PO$_4$ [8]. But these conductors are thermodynamically unstable with Li and/or cathode active materials. So the possible candidates for applications are Li$_{3.6}$Si$_{0.6}$P$_{0.4}$O$_4$, Li$_{3.8}$Si$_{0.8}$V$_{0.6}$O$_4$ and amorphous compounds in the system Li$_2$O-SiO$_2$-ZrO$_2$ because they react very slowly with Li [9]. The search for new Li$^+$ conductors has resulted in the general validity of the enhancement of ionic conductivity by orders of magnitude in dispersed two phase mixtures of LiI and Al$_2$O$_3$ or SiO$_2$ [10].

1.3.2 Sodium ion conductors

Sodium ion conductors are used in several electrochemical devices such as sodium-sulfur storage cells, electrochemical cells, electrochemical sensors and electro chromic displays. The degradation and economical problems prevent Na doped $\beta$ and $\beta''$-Al$_2$O$_3$, which were most extensively studied, from general utilization. The search for new
Na\(^+\) conductors led to the development of a new type conductor, Na\(_2\)Zr\(_2\)PSi\(_2\)O\(_{12}\) (Nasicon) [11] with a three dimensional framework structure. The compound Na\(_{3.1}\)Zr\(_{1.55}\)Si\(_2.3\)P\(_{0.7}\)O\(_{11}\) was reported to have conductivity half an order higher than that of nasicon at room temperature [12].

Other conductive phases were found in the system Na\(_{1+x}\)Y\(_x\)Zr\(_{2-x}\)(PO\(_4\))\(_3\) [13] and Na\(_{1+x}\)(Cr,In,Yb)\(_x\)Zr\(_{2-x}\)(PO\(_4\))\(_3\) [14]. Nasicon system has high conductivity and low sintering temperature, but thermodynamically unstable.

1.3.3 Proton conductors

Proton conductors have a unique feature because of the absence of an electron cloud. H\(_3\)O\(^+\)/NH\(_4\)\(^+\)β"-Al\(_2\)O\(_3\) [15] is regarded as a very promising material for use in solid electrolyte cells because of its thermal stability. Some compounds based on the composition of SrCeO\(_3\) were found to exhibit high proton conductivity [16].

1.3.4 Other cation conductors

Recently two new cations conductors with the β"-Al\(_2\)O\(_3\) structure are developed. One is polycrystalline Kβ"-Al\(_2\)O\(_3\) fabricated by vapor phase ion exchange. The other is Pb β"-Al\(_2\)O\(_3\) fabricated by liquid phase ion exchange [17]. More intense work is going on in the field of cation conductors.

1.3.5 Fluorine ion conductors

High ionic conductivities have been reported for fluorides because of certain features of fluorine ions, such as their monovalence, small size and strong ionic character. These properties make F\(^-\) conductors useful for electrochemical devices, including batteries, infrared detectors and gas sensors. Examples for F\(^-\) conductors are β-PbSnF\(_4\) [18] and NH\(_4\)Sn\(_2\)F\(_5\), which have conductivity value same as that of fast cation conductors.
Two common disadvantages of fluorides are low melting points and their tendency to be decomposed by moisture in air. It is possible to improve the conductivity by doping to produce vacancies and/or interstitial ions. However it is difficult to approach the performance of best ion conductors in the fluorides, as the introduced defects do not contribute to the conductivity because of strong interaction.

1.4 Oxide ionic conductors

In oxygen ion conductors, current flow occurs by the movement of oxide ions through the crystal lattice. This movement is a result of thermally activated hopping of the oxygen ions, moving from crystal lattice site to crystal lattice site, with a superimposed drift in the direction of the electric field. The ionic conductivity is consequently temperature dependent, but at higher temperatures can approach values close to 1 Scm\(^{-1}\) comparable to the levels of ionic conductivity found in liquid electrolytes.

This property of these solids is remarkable and to understand its origins the following observations are necessary,

1. The crystal must contain unoccupied sites equivalent to those occupied by the lattice oxygen ions.
2. The energy involved in the process of migration from one site to the unoccupied equivalent site must be small (<1eV).

The oxygen ions are the largest components of the lattice, with an ionic radius of 1.4 Å, intuitively, it would be expected that the smaller metal ions would be more likely to have an appreciable mobility in the lattice and, hence carry the current. However, in certain special and open crystal structures this is not the case and it is the oxygen ions that migrate in the electric field. Thus the materials displaying oxygen ion conductivity must have highly unusual crystal structures with partially occupied oxygen sites. Hence the number of oxide ionic conductors is relatively small.

In order to obtain a material that is a pure oxygen ion conductor (a solid electrolyte), the level of any electronic contribution to the total electrical conductivity
must be negligible. Since the mobility of electrons and holes is very high in comparison with ionic mobilities, the low concentration of electronic carriers will give rise to a significant electronic component. Most oxygen ion conductors are, in fact, mixed conductors and only very few are capable of being classed as pure ionic conductors.

In most technological applications, the oxygen ion conductors are used in extreme conditions. Under such extreme conditions, many oxides will get reduced and the reduction process will liberate electrons and give rise to electronic conductivity. Very few materials meet the stringent requirements needed to function satisfactorily as an electrolyte in a device such as a solid oxide fuel cell (SOFC) and, hence, the need to search for alternatives with superior properties [19].

Oxygen ion conductors such as ZrO$_2$, CeO$_2$, ThO$_2$ and Bi$_2$O$_3$ have been studied in detail because of their use in oxygen sensors, fuel cells and other electrochemical devices [20, 21]. New ordered phases were recently found in the system CaO- ZrO$_2$ [22] and Y$_2$O$_3$- ZrO$_2$ [23].

1.4.1 Fluorite structured oxides

The fluorite structured oxides are the classical oxygen ion conducting oxide materials. The study of these materials as electrolytes derives from the early investigations of Walter Nerst circa 1900. The crystal structure consists of a simple cubic oxygen lattice with alternate body centers occupied by eight coordinated cations. Thus, the fluorite structure consists of a face-centered-cubic cation array with anions in the tetrahedral sites [24]. The general formula of a fluorite type oxide is A$_2$O$_2$, where A is a large tetravalent cation (Fig.1.1) [19].

Some of the materials that form in the fluorite structure are uranium oxide (UO$_2$), thorium dioxide (ThO$_2$) and ceria (CeO$_2$). The Zr$^{4+}$ cation is too small to sustain the fluorite structure and only forms either at high temperatures or when the zirconium is partially doped with another (usually larger) cation.
Doping is usually performed by substituting lower valence cations into the lattice, with the added effect of introducing oxygen vacancies to maintain overall charge neutrality. These oxygen vacancies supply the equivalent sites allowing the oxygen ions to migrate which are the prerequisite for high ionic conductivity. A peculiar feature of the fluorite structure is that it is able to sustain a high degree of substitution and consequent non-stoichiometry, making these very highly disordered materials.

Doping of the fluorite oxides is usually achieved by substitution of the host cation with either a rare earth or an alkaline earth. Examples of such materials are doped zirconias such as yttria stabilized zirconia (YSZ) with general formula $\text{Zr}_{1-x}\text{Y}_x\text{O}_{2-d}$. Increasing the dopant concentration will lead to the introduction of more vacancies into the lattice and should result in higher conductivity. This correlation only applies at low concentrations of dopant and it is found that at higher concentrations of dopant the ionic conductivity is limited.

The isothermal conductivity does increase as the level of substitution increases, however, a maximum is observed at relatively low additions of the dopant because of the interactions of the substitutional cation with the charge compensating oxygen vacancy it introduces. Originally, it was thought that this was a Coulombic effect, as both the substitutional ion and the vacancy act as if they were oppositely charged species within a neutral lattice. But now it is clear that the major interaction between these point defects
is through the elastic strain introduced into the crystal lattice by the mismatch between the size of the dopant ion and the ion that it replaces. In making good oxygen ion conductors it appears that as well as introducing vacancies, leaving the crystal lattice as undisturbed as possible is highly desirable [19].

1.4.2 Perovskite structured oxides

One class of materials that exhibits high oxide ion conductivity is based upon the perovskite structure. The perovskite structure is a relatively simple crystal structure that has the ABO$_3$ stoichiometry. Typically the A-site cation is large, such as alkali, alkali earth and rare earth, and will be coordinated by the 12 anions in the lattice. The B-site cation is typically smaller and frequently transition metals like Al and Ga [25] (Fig.1.2) [19]. It will be six coordinate, forming BO$_6$ octahedra. The perovskite oxides are interesting because there are two cation sites upon which to substitute lower valence cations, leading to much wider range of possible oxygen ion conducting materials. The ideal perovskite is the cubic structure with the tolerance factor of 1.0. The tolerance factor is obtained from ionic radii as

$$t = \frac{(r_A + r_0)}{\sqrt{2} (r_B + r_0)}$$

(1.3)

where $r_A$ and $r_B$ are the mean ionic radii for A and B site cations taking into account the coordination numbers, respectively and $r_0$ is the radius of oxygen ion [26]. The perovskite structure is stable in the range of 0.75< t <1.0, and is cubic in the range t >0.95 [27]. The optimum tolerance factor to obtain the largest electrical conductivity of perovskite type oxides seems to exist near t =1 [26].
A number of perovskite oxides are purely oxide ion conductors and have been used as electrolytes in the intermediate temperature range (650-800°C). Perovskite type oxides tolerate inclusion of oxygen vacancies in the lattice, so they are sustainable as materials exhibiting high oxygen permeability. Of the perovskites investigated, the lanthanum gallate (LaGaO$_3$) based material has been found to be suitable for ionic applications.

Finally, the conditions concerning oxide ion conduction in fluorites and perovskites can be summarized as follows:

1. High concentration of mobile charge carriers, i.e., oxide ion vacancies.
2. The energy of the oxide ion sites has to be equal or only slightly different.
3. Weak bonding energy resulting in a relatively low melting point.
4. Open paths between oxide ion sites [19].

1.4.3 New oxide ion conductors recently developed

Lacorre et al. developed the LAMOX family of oxide ion conductors [29]. The materials based initially on the La$_2$Mo$_2$O$_9$ parent compound. At temperatures above 600°C there is an α-β phase transition for these materials. Associated with this transition, there is an increase in ionic conductivity by approximately two orders of magnitude. The remarkable performance of this material is attributed to the structure where electron lone pair acts as structural elements within the crystal. The Mo content of this material leaves
it susceptible to reduction and hence there have been several studies utilizing doping strategies to overcome both the reducibility of the material and the transition temperature [29].

A recent discovery in the field of ionic conductors has been the apatite structured oxides; important among them are La_{10-x}Ge_{6}O_{26+y} and La_{10-x}Si_{6}O_{26+y}. These materials have been identified as having relatively high levels of oxide ion mobility with a Sr-doped material, La_{9}SrGe_{6}O_{26.5} [30]. At lower temperature this composition has higher levels of ionic conductivity than YSZ by half an order of magnitude, but this material requires high temperature of synthesis and sintering.

The BIMEVOX family of oxide ion conductors is based on the fluorite related oxide Bi_{2}O_{3} [31]. A typical composition would be Bi_{2}M_{x}V_{1-x}O_{5.5-3x/2}, these materials are doped with a transition metal and V and have proven to be highly effective as oxygen separation membranes with ionic conductivity of the order of 0.1S cm\(^{-1}\) at 600°C. BIMEVOX family also have a phase change and recently the first isotopic exchange measurements were performed on these materials to gain direct information about the diffusion and surface exchange characteristics of these materials.

1.4.4 Applications of oxide ion conductors

Oxygen ion conductors have been with us now for over a century. The first application was by Nemst, who used stabilized zirconia as filaments in his glower electric lights, driven by the need to replace dirty and dangerous candles and gas lamps. Modern applications are also driven by considerations of clealiness, sustainability and efficiency [19].

Oxide ion conductors find application in fuel cells [32] which convert chemical energy directly into electrical energy with high efficiency compared to other systems. The solid oxide fuel cell (SOFC) is a solid state device that can generate electricity in an electrochemical cell by combining fuel and oxidant gases across an oxygen ion conducting solid electrolyte. The current technological applications of SOFCs are based upon the oxygen ion conducting yttria stabilized zirconia solid electrolyte [4].
Solid electrolytes interfaced with suitable electrodes can quantitatively transduce the ratio of activities of the ionically conducting component at the two electrodes directly into an electrical potential. This forms the basis of using solid electrolytes in the development of chemical sensors for monitoring and/or controlling chemical components in gaseous, liquid and solid systems [33]. The yttria stabilized zirconia oxygen sensors are one of the most successful applications of solid electrolytes. Oxygen ion conductors are also used in the gas sensors for SO\textsubscript{x}, NO\textsubscript{x}, CO\textsubscript{2}, HCl, CO and hydrocarbons [4].

1.4.5 Oxide ion conductors for SOFC application

Despite being first demonstrated over 160 years ago, and offering significant environmental benefits and high electrical efficiency, it is only in the last two decades that the fuel cells have offered a realistic prospect of being commercially viable. Fuel cells use some sort of chemical fuel as its energy source and directly convert it to electrical energy with high efficiency and low emission [34]. Of the different types of fuel cells such as, Alkaline Fuel Cell (AFC), Phosphoric Acid Fuel Cell (PAFC), Polymer Electrolytic Membrane (PEM) Fuel Cell, Molten Carbonate Fuel cell (MCFC) and Solid Oxide Fuel Cell (SOFC), the SOFC offers great promise and presently the subject of intense research activity since it is a solid state device and operates at elevated temperatures [35].

The primary components of solid oxide fuel cell are cathode, anode and electrolyte (fig 1.3). Fuel is fed to anode and oxidant is fed to cathode [36]. The reaction taking place in a fuel cell is given below [37].

Cathode: \( \frac{1}{2}O + 2e^- \rightarrow O^2^- \)
Anode: \( H_2 + O^2^- \rightarrow H_2O + 2e^- \)
Overall: \( \frac{1}{2}O + H_2 \rightarrow H_2O \)
Nowadays most of the research is focused on optimizing the ionic conductivity of the solid electrolyte. In this section a brief review of ionic conductors, particularly, oxygen ion conductors with fluorite and perovskite structures are presented. There are several of comprehensive reviews on recent developments of ionic conductors, based on different structures and applications [37-41].

The classic oxygen ion conductors, stabilized zirconia and ceria are based on the fluorite structure. In order to introduce mobile oxygen vacancies into the compound tri or divalent dopants are added to the host material. Almost all SOFC systems currently being developed employ an yttria stabilized zirconia electrolyte. This is because in addition to having good oxygen ion conductivity, it shows good stability in both oxidizing and reducing atmospheres and is unreactive towards other components used in the SOFC [35].

Doping zirconia with other cations stabilizes the cubic and tetragonal phases by de-stabilising the monoclinic phase [42]. For both zirconia and ceria conductivity increases with increasing dopant concentration up to some maximum value and then decreases rapidly. The conductivity increases then decreases across the rare earth series from Y to La. For zirconia, Sc gives rise to the highest conductivity [43], but ruled out on cost grounds. Yttria stabilized zirconia (YSZ) became the next choice [44]. With yttria as the dopant, the conductivity of zirconia peaks at about 8mol% dopant concentration. Fukui et al investigated the relationship between microstructure and ionic conductivity of
YSZ electrolytes [45]. Zhu et al. also studied the YSZ by varying the sintering conditions of nanosized YSZ powders [46].

Physical, chemical and electrochemical properties of pure and doped ceria were studied for practical application of it in solid state electrochemical devices [47]. Eguchi et al. studied the ceria doped with samarium and proposed that Sm doped ceria (SDC) give the highest values of conductivity and the optimal dopant concentrations are 10-20% [48]. Steele discussed the case of ceria doped with Gd and found that doping Gd to ceria (CGO) results in high value of conductivity [49]. Sammes et al. found that the CGO has a relatively narrow region of oxide ion conductivity as an electronic component is introduced on reduction [50]. Mogenson et al. explained the strong dependence of ionic conductivity on dopant type and concentration [51]. According to them this is due to the lattice distortion introduced by the dopant.

Ionic conductivity of ceria is approximately an order of magnitude greater than YSZ. This is the result of the larger ionic radius of $\text{Ce}^{4+}$ (0.87 Å) than $\text{Zr}^{4+}$ (0.72 Å), which produces more open structure trough which O ions can easily migrate. But ceria had not been considered as a realistic candidate because of its reducing conditions. Under reducing conditions CeO$_2$ becomes CeO$_{2-x}$ and n-type conductivity increases. Steele estimated the electrolytic domain boundary, the oxygen partial pressure at which electronic and ionic conductivities are equal, for 10 and 20% Gd doped ceria [49].

Milliken et al showed that reported open circuit potentials for doped ceria are lower than that expected on the basis of the electron conductivity of ceria [52]. Atkinson et al studied the challenge lies with the chemical expansion of ceria under reducing conditions and internal stress that result [53]. Christie et al studied the microstructure ionic conductivity relationships in ceria gadolina electrolytes [54]. Tompesett et al examined the reaction between YSZ and CeO$_2$ and showed the formation of 10 mol% YSZ in CeO$_2$. The structure, thermal expansion coefficient and ionic and electronic conductivities of Ce$_{1-x}$Bi$_x$O$_{2.5}$ solid solutions prepared were investigated by Dikmen et al. The conductivity obtained for this material is 1-2 order magnitude higher than that of YSZ [55].
Sammes et al took an effort to suppress the reduction of CGO by adding 8 mol% of YSZ and 3 mol% of YSZ and found the formation of a single phase in all the samples [50]. Electrical and ionic conductivity of Gd doped ceria as a function of temperature and oxygen partial pressure is measured and described by Wang et al [56]. Hong et al. discussed the lattice parameters and densities of rare earth doped ceria electrolyte. An alkali element doped CeO$_2$-Sm$_2$O$_3$ system with fluorite structure was studied by Mori et al. Calcium doped ceria based materials for intermediate temperature application was presented by Zhu et al [57]. Other rare earth doped systems were characterized by Hong et al [58]. The crystal structure of La substituted CeO$_2$ was studied by Bae et al. [59]. Electrochemical properties of SDC20 with composition Ce$_{0.8}$Sm$_{0.2}$O$_{1.9-δ}$ were reported in detail by Matsui et al [60]. This is based on crystallographic indexing.

Various co-doped ceria based electrolytes have been investigated [61]. Recent developments have been carried out on various ceria salts composite as solid electrolytes [62]. These composites showed conductivities comparable to doped ceria. Sha et al. demonstrated that rare earth co doped Ce$_{0.8}$Sm$_{0.1}$Y$_{0.1}$O$_{1.9}$ material prepared by sol-gel method could be easy to sinter at lower temperature with better electrical property [63-64]. Zhu et al. reported the low temperature SOFC applications of ceria based composites such as samarium doped ceria and alkaline carbonates and ceria-lanthanum oxide composites [65].

Perovskite structured oxide ion conducting compositions with conductivities high enough for consideration are developed recently. An indication that the perovskite could be competitive with the fluorine structure came from the observation of an order disorder transition at 930°C in Ba$_2$In$_2$O$_5$ [66]. The ABO$_3$ perovskite structure is amenable to tailoring via doping on both the A and B cation sites. The perovskite type oxides have been widely studied and reviewed by Kendall et al [67]. Lanthanum oxides are one candidate for electrolyte [40, 68]. Doping lanthanum gallate with Sr and Mg was reported by Ishihara et al and the composition is La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_{3.δ}$. The transport properties of LSGM are comparable to that scandium doped zirconia [69]. Yamamoto reported that the LSGM has good chemical stability and negligible electronic conductivity over a large range of oxygen partial pressures [70]. Ishihara et al. report that substituting half of the
Mg\(^{2+}\) in La\(_{0.9}\)Sr\(_{0.1}\)Ga\(_{0.8}\)Mg\(_{0.2}\)O\(_{3-\delta}\) [71, 72] with Co or Ni ions improves the oxide ionic conductivity significantly.

Lybye compared the conductivity of the four perovskites La\(_{0.9}\)Sr\(_{0.1}\)B\(_{0.9}\)Mg\(_{0.1}\)O\(_{3-\delta}\) (B=Al\(^{3+}\), Ga\(^{3+}\), Sc\(^{3+}\) or In\(^{3+}\)) [73]. The conductivity is extremely ionic over a wide oxygen partial pressure range at temperatures as high as 1000°C, but is not as high as that of doped ceria. The lanthanum gallates also suffers from reactivity with nickel, the typical SOFC anode electrocatalyst. To overcome this problem ceria buffer layers have been incorporated between the electrolyte and the anode [74]. The effect of microstructure on the oxygen transport of perovskite type La\(_{0.1}\)Sr\(_{0.9}\)Co\(_{0.9}\)Fe\(_{0.1}\)O\(_{3-\delta}\) (LSCF) was studied by Yin et al [75].

The importance of the size of the B site ion is evidenced by the results published on the rare earth gallates such as NdGaO\(_3\) [76] and PrGdO\(_3\) [77]. Because the oxide ion interacts strongly with the B cation [2], the optimum oxide ion conductor should be found among the A\(^{3+}\)B\(^{3+}\)O\(_3\) type of perovskites.

The ion transport of properties of bismuth oxide has received significant attention due to its phase transition which results in an increase in conductivity [78]. Sammes et al. [79] and Shuk et al. [78] studied the conductivity of (Bi\(_2\)O\(_3\))\(_{0.75}\)(Ln\(_2\)O\(_3\))\(_{0.25}\), Ln=Er or Y. The limitation of bismuth compound is its high electronic conductivity. The dc transport number determination of Nd, Yb or Gd doped SrCeO\(_3\) was described by Kosachi et al. Kumar discussed the different modes of conduction of rare earth doped perovskite such as Yb-SrCeO\(_3\) [80].

Fast oxide ion based on La\(_2\)Mo\(_2\)O\(_9\) was investigated by Lacorre et al [81]. Crystal structure of this compound is studied by Goutenoire et al [82]. Tsai et al. prepared various rare earths substituted La\(_2\)Mo\(_2\)O\(_9\) and characterized it using impedance spectroscopy, X-ray diffraction etc [83]. The Mo content of these samples leaves it susceptible to reduction and hence there have been some study to overcome the reducibility by doping [29]. Thermal and transport properties of La\(_{2-x}\)R\(_x\)Mo\(_2\)O\(_9\) (R= Nd, Gd, Y) were investigated by Georges et al [84].

The BIMEVOX family of oxide ion conductors is based on the fluorite related oxide Bi\(_2\)O\(_3\). Recently the studies on these materials were carried out to gain the
information about its performance [85]. Studies are going on in the field of oxide ion conductors for application in SOFC.

1.5 Scope of the present study

The major problems at present the ionic conductors facing are that, high operating temperature of the electrolytes, reducing nature at extreme conditions such as high temperature and oxygen atmosphere, poor stability, above all the cost of production etc. In the light of the above discussed limitations, the present work is interesting since it make an attempt to synthesize new oxide ion conductor with better conductivity at low operating temperature.

During this project it is proposed to prepare and study the properties of new ionic conductors in the systems

1. A-A' M-M'-O (A= Na or K; A'= Ca OR Sr; M= Ti or Zr; M'= Nb or Ta)
2. ARNbO6 (R= Rare Earth) and
3. Ce1-xSmxO2

The phases in the above systems will be characterized by using the methods of powder X-ray diffraction, scanning electron microscopy (SEM) and energy dispersive analysis (EDS). Powder X-ray diffraction will give an idea of the nature and structure of the phases obtained. EDS will give information on chemical composition of the phases present and SEM will show shape and size of the grains formed in the material.

The ionic conductivity of the samples obtained will be studied using Impedance Analyzer, Solatron 1260. The results obtained in all these studies would be discussed in detail in this thesis.
Reference


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