



Chapter-1

Introduction and Literature Review

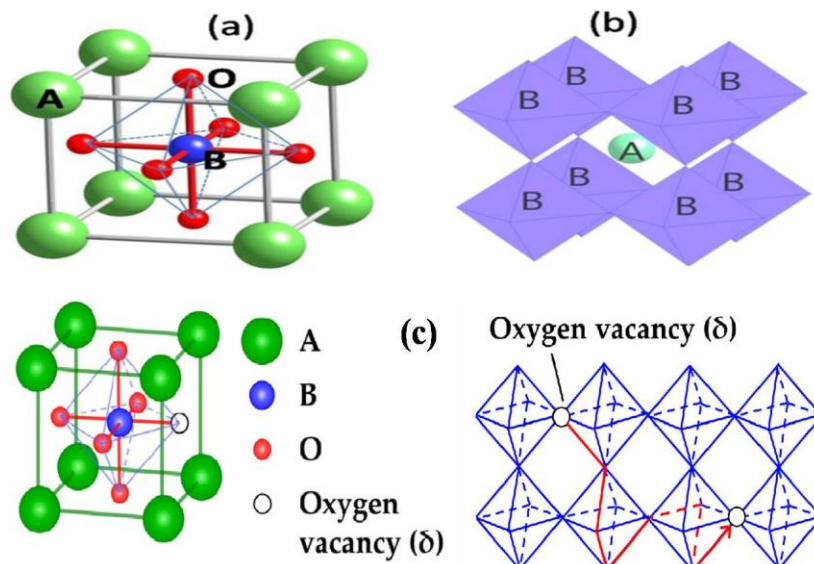
1.1 General Overview of the Field

In materials technology, the materials can be categorized in various classes such as fluorite (AO_2), rutile (TiO_2), spinel (AB_2O_4), scheelite (ABO_4), tungsten bronze (A_xWO_3), pyrochlore ($\text{A}_2\text{B}_2\text{O}_7$), perovskite (ABO_3), and double perovskites ($\text{AA}'\text{BB}'\text{O}_6$, $\text{AA}'\text{B}_2\text{O}_6$ and $\text{A}_2\text{BB}'\text{O}_6$) etc.. These structures are the most common known oxide structures and have been studied extensively. Fluorite (AO_2) based oxide materials; stabilized zirconia and doped ceria lead a group of the most important ceramic materials with various electrochemical, nuclear and ceramic applications. Fluorites are most widely used in the fields of electro-ceramics, nuclear and electrochemistry with various practical and potential applications like thermal barrier coatings, conventional and novel super-plastic and ultra-hard structural/refractory ceramics, dielectric insulators/substrates, catalysts, synthetic teeth/jewels, and solid electrolytes for oxygen sensors/monitors/pumps etc. [Nakamura et al.(2014)]. Rutile is known as the most common oxide having chemical formula TiO_2 . It shows a wide range of applications viz. TiO_2 is unique material which is widely used for application in photocatalysts for hydrogen evolution, dye sensitized solar cells, gas sensors, white pigment in paints, cosmetics, toothpastes, food colouring, and in ceramics and electric devices like varistors [Diebold (2003)]. Spinel (AB_2O_4) type materials show various interesting promising structural, optical, magnetic and electrical properties. Spinel-based materials are commonly utilized in several applications as humidity sensor devices, photocatalysts, photo luminescent materials, reinforcing fibers, nuclear technique, ceramic pigments in paints and suitable for solar cell technique [Walsh et al.(2007)]. Scheelite structure type ABO_4 based materials are used for wide range of applications on the basis of electronic-optical properties e.g. in scintillator, cherenkov detector, acousto-optic devices, stimulated Raman scattering, fiber optics and as photocatalysts [James et al.(2015)]. Tungsten bronze (A_xWO_3) based structures are especially investigated for their specific physical properties such as electrical, magnetic, electroceramic, and superconductivity [Zheng et al. (2015)]. Pyrochlore ($\text{A}_2\text{B}_2\text{O}_7$), structure exhibits some remarkable properties, with various combinations of A- and B-site cations. Pyrochlore based materials are used in several potential applications, such as: in sensors device, thermal barrier coatings, nuclear instruments, ceramic, solar cells, solid oxide fuel cells as solid electrolytes and as catalysts etc. [Christopher et al.(2002) and Lang et al. (2010)]. The perovskite and double perovskite materials exhibit various technological

applications due to their wide range of flexibility to accommodate a vast range of dopants at their regular sites. This thesis work is based on the perovskite and double perovskite materials; therefore, a brief survey of these systems is being presented in the following sections.

1.2 Perovskite Oxide Systems

In above class of materials, perovskite oxides are got special attention due to their interesting structural and physical properties viz, magnetic [Yukhno et al.(2016)]; dielectric [Arlt et al. (1985)], thermal [He et al. (2004)], catalytic [Rida et al. (2008)] electrical [Mizusaki et al.(1992)]. The perovskites are most extensively studied materials in solid state physics and chemistry [Bhalla et al. (2000)]. The perovskites are the class of materials which figure out in the form of ABO_3 , where A is an alkaline earth or rare earth cation (Ba, Ca, Sr, La etc.), and B is an electronically active transition metal cation (Mn, Fe, Co, Ni, V, Cu etc.). Generally, in these crystal structure, A- site is occupied by the larger cation at corner position and B site is occupied by the smaller cation at the body centered position and oxygen ions go to face centered position of the cubic unit cell as shown in Fig.1.1(a).



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Fig.1.1: (a) A cubic perovskite unit, cell ABO_3 , on the right, (b) corner-sharing of BO_6 octahedra in perovskite structure, ABO_3 and (c) oxygen vacancy migration path in perovskite structure, ABO_3 .

In perovskite structure, B site ions are accommodated in octahedral position (BO_6) while the A-site cations fill the unoccupied space between the corner shared BO_6 octahedra and 12 oxygen sites as illustrated in the unit cell shown in Fig.1.1(b). From the crystal geometries, it is clear that B-site cations are strongly bonded with the oxygen ions while A-site cations have comparatively weaker interactions with oxygen ions [Peter et al. (1999)].

1.2.1 Types of Perovskite Oxides

On the basis of cation valencies (A^{m+} and B^{n+}), perovskite can be classified into five sets. The criteria for perovskite arranging are the sum of the valencies of cations ($\text{A}+\text{B}$) must be equal to anions (oxygen) valencies to maintain the electro neutrality. These perovskites are described with following categories.

(a) $\text{A}^{1+} \text{B}^{5+} \text{O}_3$ Perovskite Oxides

A-site of these perovskites is occupied by monovalent cation and B-site is occupied by a pentavalent cation. Some important examples of $\text{A}^{1+} \text{B}^{5+} \text{O}_3$ type structure are LiNbO_3 , NaNbO_3 , KTaO_3 , KNbO_3 , RbTO_3 and AgNbO_3 etc. They are generally used as ferroelectric and antiferro-electric materials. KTaO_3 and KNbO_3 are used in acousto-optic and electro-optic devices while LiNbO_3 , NaNbO_3 , KNbO_3 and KTaO_3 are used in electro-optic devices, microwave surface acoustic devices and holographic memory [Smyth, 1984 (15)].

(b) $\text{A}^{2+} \text{B}^{4+} \text{O}_3$ Perovskite Oxides

In this type of perovskite oxides, A-site of perovskite is occupied by divalent cations and B-site is occupied by tetravalent cations. In electro-ceramics, a number of perovskite oxides are studied by the general formula $\text{A}^{2+} \text{B}^{4+} \text{O}_3$ where A cations are alkaline earth metal ($\text{A} = \text{Sr}$, Ba , Co , and Pb etc.) and B cations transition elements ($\text{B} = \text{Ti}$, Sn , Zr , Hf , Mo , Th etc.). Some important examples of $\text{A}^{2+} \text{B}^{4+} \text{O}_3$ series are CaTiO_3 , BaTiO_3 , and PbTiO_3 etc.. BaTiO_3 and PbTiO_3 are used as piezoelectric and ferroelectric materials. They are utilized as a piezoelectric transducer, phonograph pickups, air transducers, instrument transducers and in ultrasonic devices.

(c) $\text{A}^{3+} \text{B}^{3+} \text{O}_3$ Perovskite Oxides

In such type of perovskite oxides, both A and B cation sites are occupied by trivalent cations. Where A^{3+} cation is rare earth metal ions while B^{3+} cation is a transition metal ions, respectively. Some of the well known examples of $\text{A}^{3+} \text{B}^{3+} \text{O}_3$ type structure are BiMnO_3 ,

LnCoO_3 , LaNiO_3 , GdCoO_3 , LaCoO_3 , LaFeO_3 , LaMnO_3 , LaFeO_3 and LaCrO_3 etc.. This type of perovskite materials are extensively studied due to their fascinating structural, electrical and magnetic properties. These are more preferred potential candidates for the cathode and interconnect in solid oxide fuel cell.

(d) $\text{A}^{4+} \text{B}^{2+} \text{O}_3$ and (e) $\text{A}^{5+} \text{B}^{1+} \text{O}_3$ type perovskite oxides are not easily available in pervious reported literatures.

The tolerance factor, t , for the perovskite structure was first developed by Goldschmidt and co-workers in 1925. They established an empirical relation as

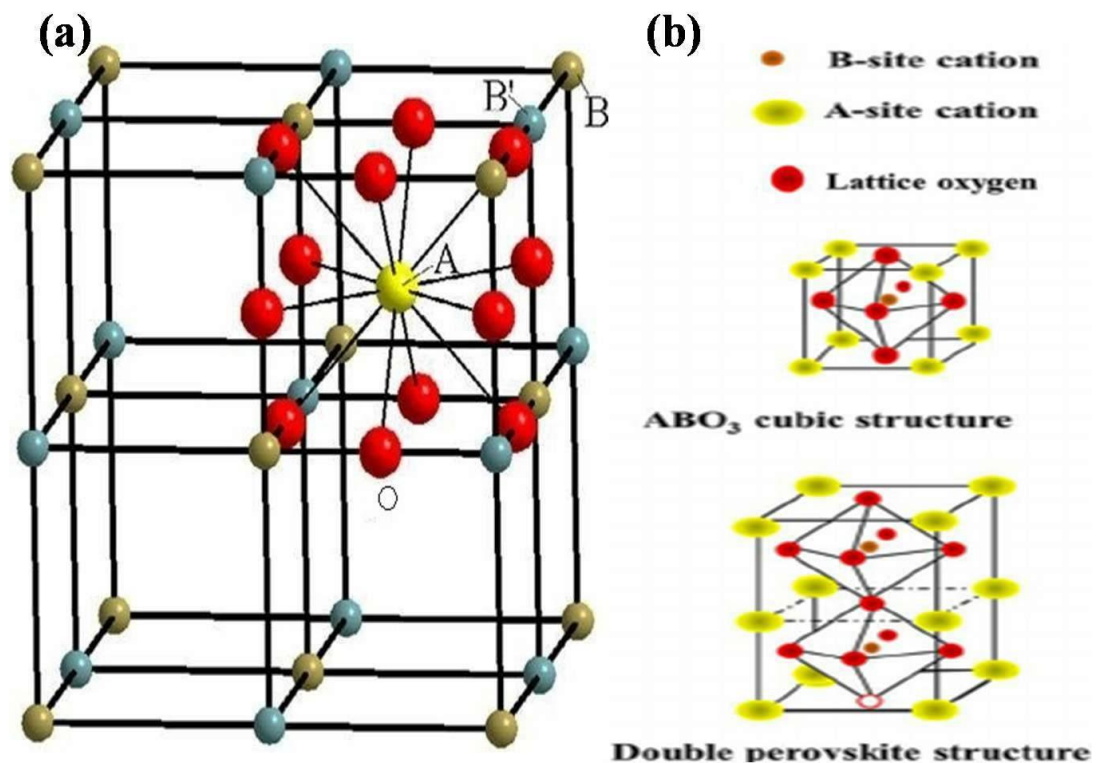
$$t = \frac{[R_A + R_O]}{\{\sqrt{2}[R_B + R_O]\}} \quad (1.1)$$

Where R_A , R_B and R_O are the ionic radii of A, B and O ions respectively in ABO_3 perovskite, t is the tolerance factor. For ideal perovskite, $t=1$. Such types of materials are typically the source of electrical conductivity. Rodriguez-Martinez et al. [1998] also reported that if tolerance factor $t \sim 1$, the perovskites ABO_3 may be enhanced their magnetic and electrical properties. Cations of the broad range of ionic radii and their valence states can able to transfer the lattice oxygen from one site to another site in the ABO_3 structure is shown in Fig.1.1(c), exhibiting the high concentrations of oxide ion vacancies and dominated higher order of ionic conductivity. This process results in to formation of oxygen vacancies and creates suitable electrical conductivity for SOFC applications. As a result of power sources; perovskite materials are highly appreciated for technological interest, electrode and electrolyte materials for solid oxide fuel cells [Bhalla et al.(2000)].

1.3 Double Perovskite Systems

The double perovskite is the class of a structural family that consists of two unit cells of perovskite structure in form of rock salt-type ordering [Vasala et al. (2015) and Patrick et al. (1997)]. The ideal double perovskite structure has a very simple arrangement of ions that is shown in Fig.1.2 (a). Double perovskite systems are represented with general formula unit of $\text{A}_2\text{BB}'\text{O}_6$ with unit cell of perovskite structures ABO_3 and $\text{AB}'\text{O}_3$ where A is either a rare earth or alkaline earth element ($A = \text{Ca, Sr, Ba}$), B is 3d heterovalent transition metal ($B = \text{Mg, Mn, Cu, Fe, Co, Ni, Cr, Cd, etc}$) and B' is a 4d transition metal ($B' = \text{Mo, Re, Sb, W, etc.}$) [Vasala et al. (2015) and Meghan et al.(2006)]. The B-site cation is separated by 50:50 ratios

of B and B' that gives a stoichiometry of $A_2BB'O_6$ structure. Two types of octahedral units viz BO_6 and $B'O_6$ are observed into the ordering of $A_2BB'O_6$ structure. The complex structure of $A_2BB'O_6$ can be constructed by ideal cubic ABO_3 with two B-site cations orders as shown in Fig.1.2 (b). There are various types of B-site cation ordering possible for stoichiometric double perovskite phase [Vasala et al. (2015)]. The stoichiometric double perovskite phase is formed by various combinations of B and B' cations with divalent A-site cations. The average B-site cations have four combinations with A^{2+} cation, which can be accomplished by a combination of B^{4+}/B^{4+} , B^{3+}/B^{5+} , B^{2+}/B^{6+} or B^{1+}/B^{7+} cations. A^{2+} cations can possess various double perovskite structure in form of $A^{2+}B^{4+}/B^{4+}O_6$, $A^{2+}B^{3+}/B^{5+}O_6$, $A^{2+}B^{2+}/B^{6+}O_6$, and $A^{2+}B^{1+}/B^{7+}O_6$. In case of A^{1+} cations, the average B-site cations have some limited combinations, such as B^{5+}/B^{5+} , B^{4+}/B^{6+} and B^{3+}/B^{7+} . Thus A^{1+} cations can make three categories of double perovskite structure in the form of $A^{1+}B^{5+}/B^{5+}O_6$, $A^{1+}B^{4+}/B^{6+}O_6$, and $A^{1+}B^{3+}/B^{7+}O_6$ [Vasala et al.(2015)].



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Fig.1.2: (a) Schematic representation of double perovskites $A_2BB'O_6$ unit cell and (b) single and double perovskite cubic structure, respectively.

All combinations of $A_2BB'O_6$ structure depend on limitations of tolerance factor t . The tolerance factor can be defined for double perovskite similar to perovskite systems. The A-site cations ordering in stoichiometric have few combinations with B^{2+} cation in form of $AA'BB'O_6$ and $AA'B_2O_6$. Several factors have been observed which affect the stability of an $AA'BB'O_6$ perovskite phase. The size miss-match between the A-site cations, the bonding preferences of the B and B'-cations, the charge difference between the B-site cations and the tolerance factor play a vital role in the stability of an $AA'BB'O_6$ perovskite [Meghan et al.(2006)]. Generally, the tolerance factor for double perovskites, with mixed A-site $A_{2-x}A'_xBB'O_6$ or $(A_{1-x/2}A'_{x/2})_2BB'O_6$, can be written as

$$t = \frac{\left[\left(1 - \frac{x}{2}\right)R_A + \left(\frac{x}{2}\right)R_{A'} + R_O\right]}{\left\{\sqrt{2}\left[\frac{R_B}{2} + \frac{R_{B'}}{2} + R_O\right]\right\}} \quad (1.2)$$

Where R_A , $R_{A'}$, R_B , $R_{B'}$ and R_O are the ionic radii of A, A', B, B' and O ions respectively in double perovskite $AA'BB'O_6$ [Popov et al. (2003)]. A site cation ordering as, A^{1+} , A^{2+} and A^{3+} are arranged with B cations in practicable range of tolerance factor $t = 0.85-1.05$. Their orientations in the three dimensions of crystal lattice are essential to determine physical presentation of double perovskite system [Prasatkhetragarn et al.(2009)]. The various arrangements of B and B' cations have been extensively studied for its electrical [Peter et al. (2011)], magnetic [Retuerto et al. (2009) and Jung et al. (1995)] and optical [Ezzahi et al. (2011), and Manounet al. (2012)] properties. These fascinating properties exhibit motivation for the study of complex and richer, double perovskite systems. Double perovskite family has been proposed for technological interest due to their various interesting properties, possible applications and its high demand as ferroelectric, piezoelectric and electrode materials for SOFC [Prasatkhetragarn et al. (2009)]. Perovskites and double perovskites are widely used as a component of solid oxide fuel cells (SOFCs). The next section discusses the materials for SOFC.

1.4 Materials for Solid Oxide Fuel Cells

Solid oxide fuel cells (SOFCs) are assembled with three layers of functional materials namely, the cathode, electrolyte and anode. The major issue, which currently limits the application of SOFCs, is their high operating temperature range (900-1100 °C) [Minh et al.

(1995), Minh (2004) and Steele (1995)]. Thus, main motive in current SOFCs research is lowering the operation temperature to the intermediate temperature range (500–800 °C) which can be achieved after development of suitable materials for cell components. Since last few decades, researchers are focused on the development of suitable materials with their appropriate processing routes. In order to develop high efficiency SOFCs, advanced materials are required which needs better processing routes [Laguna-Bercero (2012), Michael et al. (2010) and Xia et al. (2002)]. Various synthesis routes (combustion, co-precipitation, hydrothermal, sol–gel and polymeric-complexing processes) are implemented to process materials with respect to the better performance of IT-SOFCs [Shao et al. (2012)]. Recent technology has employed several advanced ceramic materials for the dynamic SOFC components. The goal of material investigation is focused on the low temperature operation (< 800 °C) as well as low cost materials for system components. The requirements of basic material properties for SOFCs are relatively stringent and well established [Minh et al.(1995), Minh (2004) and Steele(1995)]. The electrolyte materials for SOFC required enough oxygen-ion conductivity, negligible electronic conductivity, stability under both conditions (oxidizing and reducing), respectively. The porous and gas-permeable electrode (anode and cathode) materials are attributed to high electronic conductivity and remain chemically, mechanically and structurally compatible with materials of other cell components (electrolyte and interconnect). The interconnect materials that join the cathode of one cell to the anode of the next cell, must be an electronic conductor. It should remain dense and stable under both reducing and oxidizing conditions, and also chemically, mechanically and structurally compatible with materials of both electrodes (anode and cathode).

1.4.1 Cathode Materials for Solid Oxide Fuel Cells

Basic properties of cathode materials are

- High electronic conductivity.
- Chemical stability stable in environments during cell operation and fabrication of interconnection, electrolyte and fuel electrode layers.
- Thermal expansion should be matched with other cell components.
- Compatibility with the electrolyte and the interconnect.
- Sufficient porosity to facilitate transport of molecular oxygen from the gas phase to the air electrode/electrolyte interface.

The selection of the cathode material depends on the objective of applications as specific electrolyte material, the required operating temperature, the electrochemical cell design, and the specific fabrication techniques. Generally, transition-metal oxides are investigated as cathodes for SOFC because of their good electrical conductivity and comparatively low-cost as compared to alternative cathode materials. In case of high operating temperature, solid oxide fuel cells (SOFCs) prefer only noble metals or electron conducting oxides as cathode materials. The cathode materials have been classified mostly into two groups: electronic conductors (low ionic conduction) and mixed ionic-electronic conductors (MIECs). A few promising cathode materials are known as LSF (Lanthanum strontium ferrite), LSC (Lanthanum strontium cobaltite), LSCF (Lanthanum strontium cobaltite ferrite), LSMF (Lanthanum strontium manganite ferrite), SSC (Samarium strontium cobaltite), PSM (Praseodymium strontium manganite) etc.. Besides these materials some composites of cathode materials (LSM, LSF, or PSMF) with electrolyte materials (YSZ, SDC or GDC) [Stambouli et al. (2002)] are investigated. Perovskite cathode ABO_3 materials are most widely implemented cathode materials for SOFC. Among the rare earth elements, lanthanum is a widespread used which plays a vital role in the development of SOFC electrode materials, where several combinations of its oxides have fulfilled the required electronic conductivity and high catalytic activity for oxygen reduction [Bhalla et al. (2000) and Stephen et al. (2001)]. In 1966, Button et al. and in 1997 Möbiuset al. have invented $La_{1-x}Sr_xCoO_{3-\delta}$ (LSC) system and recognized as a first perovskite material to be used as cathode for SOFCs. In the series of cathode materials, lanthanum manganite ($LaMnO_3$) is the most commonly used. Typically, rare earth (e.g. Ce, Pr) doped $LaMnO_3$ have exhibited electrical conductivity [Nakamura et al. (2002)]. $La_{1-x}Sr_xMnO_{3-\delta}$ (LSM) system is a p-type conductor due to formation of cation vacancies and electronic conduction occurs from small polaron hopping conduction mechanism. This mechanism arises due to electron hole hopping between both valance states of Mn (Mn^{3+} and Mn^{4+}) [Ohno et al. (1981), Figueiredo et al. (1999) and Jacobson et al. (2010)]. The mixed ionic and electronic conducting (MIEC) perovskite oxides have been studied as cathode materials for low-temperature SOFCs [Zheng et al. (2009), Shao et al. (2004), Chen et al. (2008) and Liang et al. (2008 and 2009)]. Among the MIEC (Mixed Ionic and Electronic conductivity) cathodes, SSC ($Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$) has been reported for excellent electrocatalytic activity with better performance [Xia et al. (2002)]. In the survey of

other mixed conducting oxides, $\text{La}_{0.9}\text{Sr}_{0.1}\text{CoO}_3$, PrCoO_3 and Pr_2CoO_4 were also studied which exhibit results but their primary performance as cathode materials were frequently degraded due to formation of interfacial reaction products such as SrZrO_3 and $\text{La}_2\text{Zr}_2\text{O}_7$ [Ruiz-Trejo et al. (1998)]. In the mean time, much attention has been attributed on perovskite and double perovskite structured ceramic oxides with the speculation expectation of better cathode characteristics [Tarancón et al. (2007) and Xiao et al. (2011)]. $\text{Ln}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{FeyO}_{3-\delta}$ (LSCF) systems with $\text{Ln}=\text{Pr}$, Nd , Gd have been investigated as cathode materials due to its characteristics of mixed electronic and ionic conduction with comparable TEC (thermal expansion coefficient) to electrolyte CGO ($\text{Ce}_{1-x}\text{Gd}_x\text{O}_2$) [Sayers et al (2012), Skinner et al. (2001) and Maguirea et al. (2000)]. Besides LSCF cathode materials a series of rare earth doped $\text{Ln}_{1-x}\text{A}_x\text{Co}_{1-y}\text{B}_{1-y}\text{O}_{3-\delta}$ [$\text{Ln}=\text{La}$, Pr , Nd , Sm , Gd), ($\text{A} = \text{Sr}$, Ca , Ba) and ($\text{B} = \text{Mn}$, Cr , Fe , Co , Ni , Cu)] has been studied as the most probable cathode materials [Teraoka et al. (1985 and 1991 and 1998)]. Qui et al. [2003] reported that among $\text{Ln}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{FeyO}_{3-\delta}$, ($\text{Ln}=\text{Pr}$, Nd , Gd) systems $\text{Ln}=\text{Nd}$ system featured higher conductivity than Pr and Gd systems. Sr -doped $\text{LaCuO}_{2.5}$ system was probed as an attractive candidate for cathode materials which represented better electrical conductivity and compatible thermal expansion coefficient with YSZ electrolyte. LaNiO_3 system is not stabilized at high operating temperature, to resolve this problem Ni content was partially substituted with cobalt doping which makes it stabilized above 1000°C to use as cathode material [Rajeev et al. (1992)]. Ishihara et. al. [1995] have studied the electrochemical properties of $\text{Ln}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ ($\text{Ln}=\text{La}$, Pr , Nd , Sm , Gd , Yb , and Y) series which showed cathodic nature due to their sufficient electrical conductivity. The electrical conductivity of these perovskite materials possesses high electronic conductivity (negligible ionic conductivity).

A few Double perovskite materials have also been proved to be a good candidate for cathode application. The development of double perovskite materials such as $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_6$ (SFMO) [Xiao et al. (2011)] $\text{GdBaCo}_2\text{O}_{5+x}$ [Tarancón et al. (2007)], $\text{LnBaCo}_{1.6}\text{Ni}_{0.4}\text{O}_{5+\delta}$ ($\text{Ln} = \text{Pr}$, Nd and Sm) [Che et al.(2013)], $\text{PrBaCo}_2\text{O}_{5+x}$ [Jiang et al. (2013)], $\text{LnBaCo}_2\text{O}_{5+\delta}$ ($\text{Ln} = \text{Y}$, Pr , Nd , Sm , Gd), [Frontera et al. (2008)] $\text{SmBaCo}_2\text{O}_{5+\delta}$ [Kim et al. (2009)], $\text{NdBaCo}_2\text{O}_{5+\delta}$ [Zhao et al. (2010)] or Sr_2MMoO_6 ($\text{M} = \text{Fe}$ and Co) [Jun et al. (2014)], have also been investigated for IT-SOFCs. They exhibited high TEC values, which build them compatible with the electrolytes. Cheriti et al. [2012] have been reported that double perovskite

Sr_2MMoO_6 ($\text{M} = \text{Fe}$ and Co) systems exhibit much better cathodic performances which show a relatively high electrocatalytic activity for O_2 reduction. Jun et al. [2014] reported that the performance of $\text{SmBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{2-x}\text{Ni}_x\text{O}_{5+\delta}$ ($x = 0, 0.1, \text{ and } 0.2$) system in study of its structural, electrical and electrochemical properties suggests its application as a cathode material for IT-SOFC. Double perovskite $\text{PrBaFe}_2\text{O}_{5+\delta}$ system has been selected as cobalt-free cathode material for IT-SOFC with respect to structural, electrical and thermal properties and chemical compatibility with GDC electrolyte materials [Cheriti et al. (2012)]. Jiang et al. [2013] investigated that $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{2-x}\text{Fe}_x\text{O}_{5-\delta}$ (PBSCF) system can be applicable as cathode materials for SOFC with increasing Fe content from 0.5 to 1.5 along with decreased TEC value which could be more thermally matched with the electrolyte. Che et al. [2016] have investigated that Nickel-substituted double-perovskite, $\text{LnBaCo}_{1.6}\text{Ni}_{0.4}\text{O}_{5+\delta}$ (LnBCN) ($\text{Ln} = \text{Pr}, \text{Nd}$ and Sm) systems are potential candidates as cathode materials for IT-SOFC. The $\text{LnBaCo}_{1.6}\text{Ni}_{0.4}\text{O}_{5+\delta}$ (LnBCN) systems exhibit high chemical compatibility with samarium doped ceria (SDC) electrolyte [Xiao et al (2011)]. Zhou et al. (2008)] studied that $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_6$ (SFMO) is a promising cathode material for IT-SOFC and compatible with electrolyte $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.87}\text{Mg}_{0.13}\text{O}_3$ (LSGM).

Besides these families of materials some other materials have been considered as alternative cathode materials for IT-SOFC such as (i) brownmillerite $\text{Sr}_2\text{Fe}_2\text{O}_5$, (ii) pyrochlore-structured with a general formula $\text{A}_2\text{B}_2\text{O}_7$ (e.g., $\text{Bi}_2\text{Ru}_2\text{O}_7$, $\text{Pb}_2\text{Ru}_2\text{O}_7$, $\text{Gd}_{2-x}\text{La}_x\text{Zr}_2\text{O}_7$), (iii) layered cuprates such as $\text{LaBaCuMO}_{5+\delta}$ ($\text{M} = \text{Fe}, \text{Co}$) and $\text{YSr}_2\text{Cu}_2\text{MO}_{7+\delta}$ ($\text{M} = \text{Fe}, \text{Co}$), (iv) bismuth oxides based: $\text{Bi}_4\text{V}_2\text{O}_{11}$ Aurivillius family (BIMEVOX-based composites), (v) tetrahedrally coordinated Co compounds (Td-Co) such as $\text{RBa}(\text{Co}, \text{M})_4\text{O}_7$ (with $\text{R} = \text{Y}, \text{Ca}, \text{In}$ and $\text{M} = \text{Zn}, \text{Fe}, \text{Al}$), (vi) spinel-structured compounds such as $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$, (vii) rutile-structured compounds such as $\text{Ir}_{0.5}\text{Mn}_{0.5}\text{O}_2$ and other, more complex intergrowth structures (e.g., $\text{Sr}_4\text{Fe}_6\text{O}_{12+\delta}$, $\text{Ba}_{1.6}\text{Ca}_{2.3}\text{Y}_{1.1}\text{Fe}_5\text{O}_{13}$) etc.. [Tarancón et al. (2010), Aguadero et al. (2012), Manthiram et al. (2011) and Orera et al. (2010)]

1.4.2 Electrolyte Materials for Solid Oxide Fuel Cells

The necessary and sufficient conditions for electrolyte are its high ionic conductivity and negligible electronic conductivity that represent the stability under both oxidizing and reducing conditions and to be dense during cell operation [Hui et al. (2007)]. The conduction mechanism in solid electrolyte occurs due to the mobile charge carriers of oxygen ions (O^{2-}).

The oxide ion conduction is attributed to oxygen ion vacancy and hopping mechanism which depends on thermal activation process. To attain a high order ionic conductivity of electrolyte materials, it must acquire large interionic open space in their crystal lattice which permits an appropriate level of point defect disorder, and ground level migration enthalpy 61 eV [Xia et al. (2000)]. Badwal et al. [1996] reported that high-efficiency fuel cells electrolytes is required to develop sufficient oxygen-ion conductivity ($> 0.05 \text{ S cm}^{-1}$) at the working temperature and remain ionic conductors under oxidising and reducing atmospheres. A few well-known electrolyte materials have been investigated as Zirconia based [SSZ (Samarium stabilized zirconia), YSZ (Yttria stabilized zirconia) and CSZ (Cerium stabilized zirconia)], Sm/Gd doped ceria (SDC/GDC), LSGM, SDC nanocomposites, CDC (Cerium doped with calcium), BCN (Barium Cerate), YDC (Yttrium-doped Ceria) and LaCoO_3 based etc. Rare earth doped Zirconia oxide (ZrO_2) has been found to be one of the most attractive materials since last three decades which is demanded more due to its good electrical behaviour [Badwal (2000)]. These materials are paid the more attention by materials scientists and engineers for its applications as electrolyte materials in solid oxide fuel cells (SOFC) [Etsell and Flengas (1970), Copel et al. (2004) and Garcia-Barriocanal et al. (2008)]. Pure zirconia shows three multi forms; one of them monoclinic form stable at room temperature, above $1170 \text{ }^\circ\text{C}$, second one tetragonal form becomes stable followed by a stable cubic form above $2370 \text{ }^\circ\text{C}$. During heating treatment, the phase transformation monoclinic to tetragonal and tetragonal to cubic phase occurs at $1170 \text{ }^\circ\text{C}$ and $2370 \text{ }^\circ\text{C}$, respectively [Badwal (2000)]. Sr^{2+} and Mg^{2+} doped LaGaO_3 (Lanthanum gallate) system is a good oxygen-ion conductor. The electrical behaviour of LaGaO_3 has been explained with doping on the La^{3+} and Ga sites of Sr^{2+} and Mg^{2+} [Goldschmidt and Oslo, (1926)]. The electrical properties of LSGM system can also be adapted by partial substitution on the Ga site via transition metals such as Cr, Mn, Fe, Co, and Ni, respectively. Various transition metals doping (like Co, Ni, Fe etc.) on Ga site in LSGM have slightly improved electrical conductivity and the performance of the system [Trofimenko et al. (1999) and Ishihara et al. (2004)]. Raghvendra et al. [2014] also reported that the electrical conductivity of Ba doped LSGM system was found to increase slightly first up to $x=0.07$ and subsequently it decreased for higher dopant concentrations. $\text{La}_2\text{Mo}_2\text{O}_9$ -based ceramics are used as conventional electrolyte materials for SOFCs [Lacorre et al. (2000), and Collado et al., (2002)]. To attain high purity and high density of $\text{La}_2\text{Mo}_2\text{O}_9$ system, the

preparation routes of nano-crystalline powders have been proven to be a better option [Lopez et al. (2005)], as the nano-crystalline powder materials provide faster densification kinetics, lower sintering temperatures, high specific surface area, better mechanical and electrical properties of the electrolytes [Lopez et al. (2005), Lopez et al. (2004) and Basu et al. (2004)]. Sol-gel and freeze-dried precursor synthesis processes are suitable to achieve dense samples of $\text{La}_2\text{Mo}_2\text{O}_9$, but to attain high conductivity the sintering temperature should be increased by more than $950\text{ }^\circ\text{C}$ [Lopez et al. (2005), and Basu et al. (2004)]. The SDC, YSZ systems are investigated as composite electrolyte materials for SOFCs. The improvement in oxygen ion conductivity is initially explained by interface conduction mechanism. Mishima et al. (1998) have studied the samarium doped ceria (SDC)-YSZ composite electrolyte, and they observed that the addition of SDC demonstrates the enhancement in electrical conductivity of the composite electrolyte. Kim and his collaborators [Kim et al. (2002)] have fabricated the composite electrolytes for low-temperature SOFCs with coating the YSZ sol on tape-casted substrates YDC and GDC. It was already reported that the SDC-LSGM composite electrolyte system allows the highest ionic conductivity for particular weight ratio 9:1 [Xu et al. (2007)]. The electrical conductivity of composite electrolyte LSGM-YSZ with 9:1 ratio was enhanced in comparison to LSGM and YSZ systems [Raghvendra et al. (2014)]. For similar weight ratio (9:1), LSGM and Gadolinium-Doped Ceria (CGO) composite system was found to show highest electrical conductivity [Jo et al. (2010)]. Besides, Li et al. [2010] have reported similar result for LSGM: SDC composite system for similar weight ratio (9:1). However, Hao et al. [2012] have briefly described that SDC-LSGM electrolyte reveals maximum electrical conductivity and power density for weight ratio 9.5:0.5.

1.4.3 Interconnect Materials for Solid Oxide Fuel Cells

The most important function of interconnects is to unite the fuel cells stack in an electrical series, which provides the conductive path for electrical current to pass between the electrodes (cathode and anode). This indicates that interconnect material must require high electrical conductivity. Several interesting metallic and oxide materials are investigated as interconnect materials for SOFC. Interconnect materials under study must be mechanically and chemically stable under oxidizing and reducing atmospheres at the cathode and anode respectively, which remains to be a challenging task for these materials. The TEC (thermal expansion coefficient) of interconnect materials should be matched with other cell

components. Basic requirements for the interconnect materials under high temperature reducing (oxidizing and reducing) atmosphere [Minh (1993)]

- High chemical and physical stability
- High electronic conductivity and low oxide-ion conductivity
- High sinterability in air
- Very high density (no open porosity)
- High creep resistances for planar constructions
- Good thermal conductivity
- Good thermal expansion compatibility with other cell components

A Few prominent interconnect materials for SOFCs are: Lanthanum chromite-based (LaCrO_3); Fe–Cr based alloys, Ni–Cr-based alloys, Cr-based alloys and ferritic stainless steels etc. The materials selection criteria of interconnect are more significant and tougher than other cell components. The material selections trend of SOFC interconnect also depend on metallic and ceramic materials [Sakai et al. (2004)]. Perovskite-based LaCrO_3 materials are widely used as the ceramic interconnect for SOFCs which attributes to its thermal or chemical stability and high electrical conductivity under both reducing and oxidizing environments [Fergus et al. (2004)]. LaCrO_3 is studied as a potential interconnect material for tubular-category SOFCs operating at high temperature. Akashi et. al. [2003] and Hilpert et al. [2009] also reported that LaCrO_3 is a p-type semiconductor material under oxidizing conditions and is stable in low PO_2 situations, e.g., 10^{-16} Pa at 1000°C . Alkaline-earth-doped LaCrO_3 faced their poor sinterability in the air which is attributed to the high vapour pressure of unstable chromium element [Nakamura et al. (1979) and Anderson et al. (1978)]. The presence of Cr^{3+} and Cr^{4+} in LaCrO_3 reveals that electronic conduction occurs due to small polaron hopping mechanism [Hilpert et al. (2003), Zuev et al. (2002), Anderson et al. (1985-89), Yasuda et al. (1995) and Zhong (2006)]. As interconnect materials LaCrO_3 faces various problems such as poor sinterability in the air due volatilization of chromium, mismatched thermal expansion coefficient (TEC) with other cell components of SOFC and lack of high conductivity [Zhong (2006)]. Alkaline earth (Ca, Mg, Sr, etc.) doped LaCrO_3 system improves its electrical conductivity. Ca-doped yttrium chromite has better thermal expansion compatibility, mainly in reducing environments [Yeong-Shyung and Armstrong, (2000)]. In operating temperature

range 900-1000 °C interconnects made of nickel based alloys as inconel 600 are possible [Matsuzaki and Yasuda et al. (2001)]. In case below 800 °C, ferritic steels can be used and below 700 °C it becomes possible to use stainless steels, which are relatively economical and readily available [Ralph et al. (1999)]. In the comparison of perovskite interconnect materials, Ni–Cr- or Ni–Fe–Cr-based alloys are usually much stronger and existing more oxidation resistant during operation of SOFC interconnects [Yang et al. (2003) and England et al. (1919)]. Doped LaCrO₃ based interconnect are replaced by a metallic one due to the reduction of operating temperature below 800 °C. SrTiO₃-based perovskites are considered as more attractive new potential candidates for interconnect in SOFC. As interconnect, SrTiO₃ perovskite has also good chemical and physical stability under both atmospheres (oxidizing and reducing) [Chan et al. (1981)]. Tsukuda [2009] and Tomida et al. [2009] have investigated that La³⁺ doped SrTiO₃ system can be assumed as an interconnect material in segmented-in-series tubular SOFCs. Mori et al. [2011] also reported that doping of Ti site with Co in SrTiO₃ system is also achieved the requirements of interconnect materials for SOFC.

1.4.4 Prominent Anode Materials for Solid Oxide Fuel Cells

The basic requirements for a SOFC anode materials are relatively similar to those for cathodes (except reducing environment as place of the oxidizing environment), with appropriate electronic conductivity, thermomechanical and chemical compatibility with the electrolyte and interconnect materials, necessitated porosity to allow gas transport to the reaction sites.

Basic properties and characteristics of anode materials:

- High electronic and low ionic conductivity
- High porosity
- Large triple phase boundary
- Stable in a reducing atmosphere
- Compatible to electrolyte (Thermal Expansion Coefficient should match with neighbouring cell component)

Most of materials such as conductive oxides have been used as possible SOFC anode materials. Ceria based anode materials have been also widely investigated for lowering the operating temperature. Doped CeO₂ represents mixed ionic and electronic conductivity in a

reducing atmosphere due the presence of mixed balance state of Ce (Ce^{4+} and Ce^{3+}) [Fergus et al. (2006)]. CeO_2 based some composites, Cu– CeO_2 , Ni–CGO, Cu–Ni–CGO, and Cu–CGO also preferred as anode materials for SOFC [Shaikh et al. (2015)]. As another fluorite materials, zirconia based ceramics are most widely used for potential anode material for SOFC. Generally, stabilized zirconia is a pure ionic conductor in SOFC fuel atmospheres, so doping is required to improve electronic conductivity. Niobium-doped zirconia has also been proposed as an SOFC anode material [Irvine et al. (1997)]. Tungsten bronze based materials were also studied as potential SOFC anodes. Tao et al. [2004] also investigated that tungsten bronze structure can be obtained from the perovskite by rotation of some of Ti/NbO_6 octahedra. Among the various transition metals $(\text{Ba, Sr, Ca, La})_{0.6}\text{M}_x\text{Nb}_{1-x}\text{O}_3$ ($\text{M} = \text{Ni, Mg, Mn, Fe, Cr, In, Sn}$) compositions, $\text{Sr}_{0.2}\text{Ba}_{0.4}\text{Ti}_{0.2}\text{Nb}_{0.8}\text{O}_3$ shows the highest conductivity (10 S/cm at $p\text{O}_2 = 10\text{-}20$ atm at 930°C) [Slater et al. (1999) and Kaiser et al. (2000)]. The pyrochlore structures that contains some small empty A sites have also been proposed as anode materials. It can also be considered as a perovskite-related phase with little extra oxygen in the lattice. It was also investigated that some materials with pyrochlore structure exhibit high ionic conductivity [Tao et al. (2004)]. Poart et al. [1996] reported that mixed valence state of transition elements, such as manganese into $\text{Gd}_2\text{Ti}_2\text{O}_7$ system increase the electronic conductivity, but this was unsuccessful. $\text{Gd}_2\text{Mo}_2\text{O}_7$ system under anodic conditions exhibits metallic-like electrical conductivities of the order of 10^2 S/cm at room temperature [Subramanian et al. (1983)]. Holtappels et al. [2000] have been observed that the electrical conductivity of pyrochlore $\text{Pr}_2\text{Zr}_2\text{O}_7$ system modified on the B-site with 5% Mn or 20% Ce was lower than 2×10^{-3} S/cm⁻¹ at 1000°C in $\text{H}_2/\text{H}_2\text{O}$ atmosphere. Since the present thesis is devoted to the perovskite and double perovskite-based anode materials, therefore it is worthwhile to discuss these systems in detail.

1.5 Perovskite and Double Perovskite Anode Materials

1.5.1 Perovskite Anode Materials

The present overview is on basic characterizations (structural and electrical conductivity) of perovskite material for a specific application as a function of compositions and the type of magnitude which affect their properties. The importance of perovskite is summarized in terms of structural and electrical conductivity and classified the perovskite based anode materials for SOFC. Perovskite is a most important unit of materials that represents the suitable

properties for several technological applications. These are being extensively studied over the last few decades for their rich multiplicity of electrical, dielectric, magnetic and optical properties [Vasala et al. (2015)]. During the last two decades, studies on the electrical properties of perovskite materials have produced enormous information on electro-ceramic materials. Perovskite structure can stand for wide-ranging modifications by substituting the A and/or the B-site cations of the ABO_3 to improve specific properties such as electrical conductivity, catalytic activity, thermal compatibility, and stability, respectively. These activities lead to several substances which are considered to be potential anode materials for SOFC. Perovskite compounds such as $LaCrO_3$ [Bao et al. (2008) and Jiang et al. (2008)], $SrTiO_3$ [Zhou et al. (2014) and Sun et al. (2008)], and $BaTiO_3$ [Wang et al. (2009) and Ding et al. (2008)] are generally used as electro-ceramic compounds. Perovskite structures can go through wide variations of the doping elements at the A and B sites with much more complex compositions. Our study is especially concerned with the electrical properties in perovskite systems under investigation.

In renewable energy applications, most of the chromite-based perovskite materials have been investigated. In view of their remarkable electrical performance, chromite-based perovskite structure played a key role in the development of electrode materials for SOFC. Some specific chromite-based perovskite ceramics are being appreciated as a potential candidate for anode materials in SOFCs. $SrTiO_3$ based compounds have shown excellent photocatalytic properties [Sun et al. (2008) and Vasala et al. (2015)].

In advanced ceramic materials, lanthanum chromite ($LaCrO_3$) is the most suitable candidate to develop it as anode materials for SOFC due to its long-term stability and reliability along with long durability [Jiang et al. (2008)]. It exhibits high electronic conductivity and excellent photocatalytic behaviour in both reducing and oxidizing atmospheres. It also reveals fairly good compatibility with other cell components. In SOFC configuration, the doped $LaCrO_3$ is still the most broadly used materials for an anode and interconnect [Jiang et al. (2008)]. A wide range of study of electrical properties of $LaCrO_3$ system has been investigated and reported in the literature with the description of pure and doped forms. Dong et al. [2012] reported that Ce-doped $LaCrO_3$ is a potential anode material for SOFC. It has been studied that lanthanum chromite with doping of alkaline earth elements also represents high p-type conductivity [Akashi et al. (2003)]. Moreover, in $La_{1-x}M_xCrO_3$

(with M = Mg, Ca, Ba, Sr) systems, it has been reported that Ca and Sr doped compositions showed highest conductivities [Jiang et al. (2008)]. Mukherjee et al. [2012] also reported that Ca-doped LaCrO₃ was found thermally activated with small hole-polaron hopping conduction mechanism and shows that electrical conductivity decreases with increasing Ca concentration.

Table.1.1 *Electrical conductivity of some chromite and titanate-based perovskite ceramic materials in reducing atmosphere:*

Compositions	Electrical conductivity(Scm ⁻¹) (Reducing atmosphere)	References
La _{0.7} Mg _{0.3} CrO ₃	~0.17	Jiang et al.(2008)
La _{0.7} Sr _{0.3} Cr _{0.5} Ti _{0.5} O ₃	~0.02	Pudmich et al.(2000)
La _{0.8} Sr _{0.2} Cr _{0.5} Mn _{0.5} O ₃	~1.3	Tao et al. (2003)
La _{0.75} Sr _{0.25} Cr _{0.5} Mn _{0.5} O ₃	~0.22	Jiang et al.(2008)
La _{0.7} Ca _{0.3} TiO ₃	~2.7	Pudmich et al.(2000)
La _{0.4} Sr _{0.4} TiO ₃	~96	Neagu et al. (2010)
La _{0.1} Sr _{0.9} TiO ₃	~3	Marina et al. (2002)
Sr _{0.895} Y _{0.07} TiO ₃	~7–64	Vozdecky et al. (2011)

1.5.2 Double Perovskite Anode Materials

Molybdenum (Mo) based double perovskite ceramics have featured properties for anode materials of SOFC. Such type element has preferred only a +6 valence state at normal oxidized condition. This has been studied in a large valence range from 0 to 6. The double perovskite series in form of Sr₂MMoO_{6-δ} (M = Mn, Fe, Co, Ni, Cr etc.) systems, having applications in electroceramics [Rad et al. (2015)], very high conducting oxides [Mahato et al. (2015) and Cowin et al. (2011)], and catalysis [Li et al. (2011)]. In molybdenum-based double perovskites, Mo is also taking place the B site, but Mo⁶⁺ or Mo⁵⁺ is paired with 2+ or 3+ valence ions respectively. Mo-based double perovskites face major challenges due to the formation of additional secondary phases. The investigated additional phases affect the structural and electrical properties of such type of materials in the positive or negative way. Generally, SrMoO₄ phase is observed in Sr₂MMoO_{6-δ} (M = Mg, Fe, Mn, Co, Ni, Zn) systems [Vasala et al. (2010-11) and Filonova et al. (2014)]. This additional SrMoO₄ phase in

$\text{Sr}_2\text{NiMoO}_6$ system could be eliminated with the extra addition of NiO (5 wt%) [Prasatkhetragarn et al.(2009)]. Vasala et al. (2010)] reported that the observed phase impurity of SrMoO_4 in $\text{Sr}_2\text{MgMoO}_6$ system enhances the electrical conductivity due to subsequent reduction of SrMoO_4 into SrMoO_3 in anodic condition. Also, the presence of SrMoO_4 phase suppresses the evaporation of Mo at the stage of high temperature synthesis of $\text{Sr}_2\text{MgMoO}_6$ system [Vasala et al. (2011)]. In Mo-based double perovskites, a few extra phases have been observed as SrMoO_4 , Sr_3MoO_6 , SrMoO_3 , Sr_2MoO_4 , Ni and MoNi_4 which can change the result of electrical conductivity and the catalytic properties [Filonova et al. (2013) and Graves et al. (2010)]. This class of materials show mixed conduction i.e. electronic as well as ionic conduction [Prasatkhetragarn et al. (2009)]. When the crystals of these materials release the oxygen, it produces oxygen vacancies and electrons that play a crucial role in conduction mechanism. Both valences (6+ and 2+) ions in the Mo-based structure must have coordination flexibility to permit release of oxygen from the crystal lattice arrangements [Li et al. (2011)].

The electrical conductivity of double perovskites varies extensively depending on the 6+/2+ or 5+/3+ ordering of crystal lattice. Among these, Ni-Mo based alloy electrodes with fine micro-structures have been reported for highly catalytic activity and better performance as negative-electrodes in alkaline electrolysis cells. Dorai et. al. [2013] reported that Fe doping in $\text{Sr}_2\text{MgMoO}_{6-\delta}$ system increased the electrical conductivity with increasing doping concentration. In $\text{Sr}_{2-x}\text{MgMoO}_{6-\delta}$ system, Mn substitution on Mg site enhanced the catalytic activity with increase of Mn concentration [Li et al. (2011)]. Goodenough et al. [2009] also reported that Ni and Co variant double-perovskites, SNM ($\text{Sr}_2\text{NiMoO}_6$) and SCM ($\text{Sr}_2\text{CoMoO}_6$), revealed anomalous conductivity performance in reducing atmosphere. In the study of SNM, electrical conductivity has been observed in the range of $\sim 0.1\text{-}250 \text{ Scm}^{-1}$ under various reducing atmospheres [Zuev et al. (2002)]. The better performance of SNM is mainly due to its high catalytic activity and stability as compare to SCM.

Some of the rare-earth doped double perovskites show good performance as anode materials and also motivated IT-SOFCs due to their mixed electronic and ionic conductivity [Savaniu et al. (2011), Zhang et al. (2011), Nague et al. (2011) and Xie et al. (2011)]. Various rare-earth (La^{3+} , Sm^{3+} , Al^{3+}) doping on Sr-site get better electro-catalytic activity that plays a

key role in better fuel oxidation and electrochemical performance [Xie et al. (2011), Jiang et al. (2014), Ji et al. (2007) and Zhang et al. (2011)].

Table.1.2 Electrical conductivity of some molybdenum based double perovskites.

Molybdenum based double perovskites	$\sigma(\text{Scm}^{-1})$ (Reducing atmosphere)	References
$\text{Sr}_2\text{MgMoO}_6$	~4–8	Huang et al. (2006)
$\text{Sr}_2\text{Mg}_{0.95}\text{Al}_{0.05}\text{MoO}_6$	~5.3	Xie et al. (2011)
$\text{Sr}_2\text{CoMoO}_6$	~1.17	Zhang et al. (2011)
$\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_6$	~310	Liu et al. (2010)
$\text{Sr}_2\text{Fe}_{4/3}\text{Mo}_{2/3}\text{O}_6$	~16	Xiao et al. (2010)
$\text{Ca}_2\text{FeMoO}_6$	~416	Zhang et al. (2010)
$\text{Sr}_2\text{NiMoO}_6$	~1.11	Huan et al. (2009)

1.6 Conduction Mechanism in the Perovskite and Double Perovskite Systems

Generally, electrical conductivity in electro-ceramics is a sum of ionic and electronic conductivity that approaches to the applicability of ceramic materials for applications. Electrical conduction also depends on charge carriers of electrons, holes and oxygen vacancies that can be summarized as the mobility of charge carriers as follows Nerst-Einstein relation

$$\sigma' = ne\mu_e + p e \mu_h + 2e [V_{O}^{\bullet\bullet}] \mu_{V_{O}^{\bullet\bullet}} \quad (1.3)$$

where μ_e , μ_h and $\mu_{V_{O}^{\bullet\bullet}}$ are the mobilities of electrons, holes and oxygen vacancies, respectively. The oxygen vacancies are created at higher temperatures and the electronic carriers are generated due to the charge compensation processes leading to the enhancement in conductivity with increasing temperature [Mason et al. (2016)]. To explain conduction mechanism of perovskite and double perovskite systems, numerous defect equations can be considered [Jiang et al. (2008) and Xie et al. (2011)]. These are based on the structural, thermal and/or electrical properties of pure non-stoichiometric oxides, doped-stoichiometric oxides and doped-non stoichiometric oxide systems. Wide spread studies have been initiated to determine the conduction progression with the help of defect chemistry that attributed mainly via effect of ionic radius, valence, and concentration.

1.6.1 Ionic Conduction

The ionic conductivity σ_i in perovskite and double perovskite systems depends mainly upon various factors, such as sample preparation, temperature, dopants concentration, defect dissociation and oxygen partial pressure etc.. The dependence of ionic conductivity, σ_i on temperature, T can be represented by Arrhenius relation

$$\sigma_i T = A \exp\left(-\frac{E_a}{kT}\right) \quad (1.4)$$

where A is pre-exponential factor, k is Boltzmann constant and E_a is activation energy for ionic conduction, respectively. Ionic conductivity for any given material can be explained in terms of charge carrier concentration C_i , ionic mobility μ_i and charge q_i of the charge carriers [Mahato et al. (2015)]. This correlation can be given as

$$\sigma_i = C_i q_i \mu_i \quad (1.5)$$

The concentration of oxide ions in terms of oxygen vacancy ($V_{O}^{\bullet\bullet}$) can be written as

$$C_i = (1 - [V_{O}^{\bullet\bullet}]) N_0 \quad (1.6)$$

Where N_0 is number of oxide ions present in crystal lattice per unit cell volume. The ionic mobility, μ_i with ion diffusivity (D_i) may be expressed by the following Nerst-Einstein relation

$$\mu_i = \frac{q_i D_i}{kT} \quad (1.7)$$

Diffusivity is considered to be a function of activation enthalpy (ΔH_m) and activation entropy (ΔS_m), then a relation of mobility is described by the following relation

$$D_i = a^2 \vartheta_0 [V_{O}^{\bullet\bullet}] N_0 \exp\left(\frac{\Delta S_m}{K}\right) \exp\left(-\frac{\Delta H_m}{kT}\right) \quad (1.8)$$

Where a is jump distance of ion, ϑ_0 is vibration frequency of lattice. Since C_v , is represented as:

$$C_v = [V_{O}^{\bullet\bullet}] \{1 - [V_{O}^{\bullet\bullet}]\} N_0 \quad (1.9)$$

From equation of (1.7), (1.8) and (1.9) Arrhenius relation is stand for following relation

$$\sigma_i T = A [V_{O}^{\bullet\bullet}] (1 - [V_{O}^{\bullet\bullet}]) \exp\left(-\frac{\Delta H_m}{kT}\right) \quad (1.10)$$

where A is a parameter and represented as

$$A = \frac{4e^2}{k} a^2 \vartheta_0 [V_{O}^{\bullet\bullet}] N_0 \exp\left(\frac{\Delta S_m}{K}\right) \quad (1.11)$$

For less majority of $[V_o^{\bullet\bullet}]$

$$\sigma_i T = A[V_o^{\bullet\bullet}] \exp\left(-\frac{\Delta H_m}{KT}\right) \quad (1.12)$$

This relation is described the temperature dependence ionic conductivity as an exponential function [Mahato et al. (2015)].

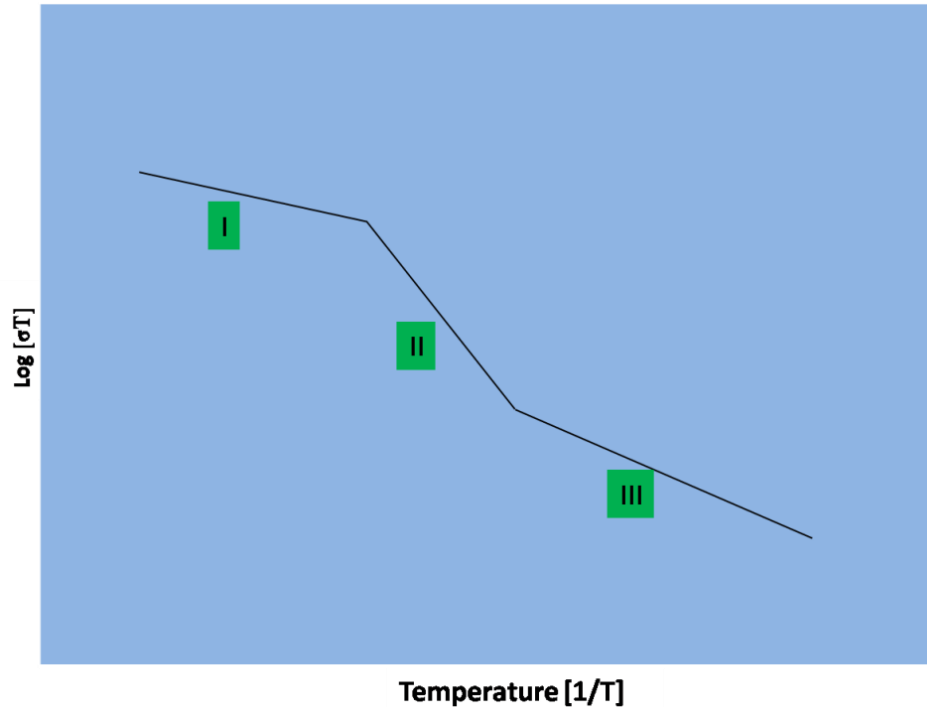


Fig.1.3: A schematic representation of the conductivity behaviour of an oxide ion conductor.

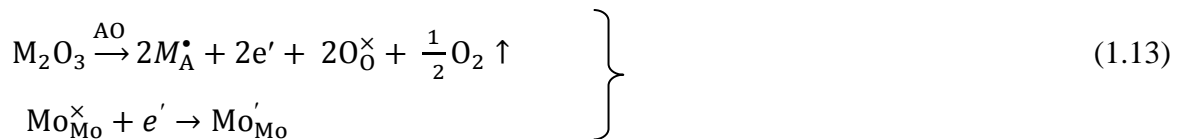
Arrhenius relation (temperature dependence) of the electrical conductivity of doped perovskite oxide cannot be expressed by a single exponential function shown in Eqs. (1.4), (1.10) or (1.12). Generally, the usual temperature dependence electrical conductivity can be shown (see Fig.1.3) in the three reasonable sections according to Kilner et al. [1982]. In first (I) region, which appears at high temperature, the electrical conduction is verified by the intrinsic defects (Schottky or Frenkel) in the crystal lattice. In second (II) region, electrical conduction is directly controlled by the majority of charge-carrying defects occurred by an aliovalent dopant ions or impurity. In third (III) region, as a guideline at low temperatures, the charge carrier's majority carrying defects is determined by the thermodynamic equilibrium between the free defects and the associated pairs. In view of these facts that doped perovskite oxides have a large number of oxygen vacancies, they just have the regions II and III, respectively.

1.6.2 Electronic Conduction

Electronic conduction is the channel of free electrons for all the way through a material. In ceramics materials, the ionic bonds gripping the atoms together do not permit for free electrons. On the other hand, in few impurities cases of different doping valence which possesses different numbers of bonding electrons in the material, and these impurities may act as donors or acceptors of electrons. In cases of rare-earth or transition metal elements of variable valency may be incorporated; such type of impurities may act as centres for polarons species of electrons that make small regions of local polarization as they move from atom to atom. Generally, electronically conductive ceramics are used in applications of resistors, electrodes, and heating elements.

Defect chemistry plays a key role to understand the electronic conduction mechanism from Kröger–Vink notation that illustrates the deviations from stoichiometry. During heating treatment, the sample loses oxygen and the oxygen nonstoichiometry which is assigned by oxygen vacancies ($V_O^{\bullet\bullet}$). Electronic conduction is studied with similar procedure and formula as ionic that is separated by limit of activation energy. Ishihara et al. (2009) and Orlovskaya et al. (2003) also reported that in perovskite structure (ABO_3), B-site transition metal is predominant for electronic conduction.

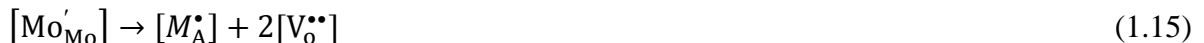
Xie et al. [2011] reported that the electronic conduction in Mo-based double perovskite enhances with trivalent cation (M^{3+}) doping of at a divalent (A^{2+}) site. It was attributed to the decrease in lattice oxygen due to the formation of electronic charge. This can be understood from the following defect Eqns.



According to the equation lattice oxygen has been lost in reducing environment generating the oxygen vacancies and reduction of Mo^{6+} to Mo^{5+} ions for the electrovalent compensation, which can be explained by the following eqⁿ.



where Mo'_{Mo} indicates the substitution of Mo^{6+} by Mo^{5+} . The electro-neutrality condition will be maintained by following eqⁿ.



The substitution of M^{3+} on A^{2+} cation site will result in decrease of oxygen vacancies and/or an increase of Mo'_{Mo} concentration (from eqⁿ. (1.15)). This will lead to an enhancement in electronic conductivity and decrease in ionic conductivity.

1.7 Effect of Doping on Electrical Conductivity of Perovskite and Double Perovskite Anode Materials

Several doped perovskites and double perovskites structures were investigated for better performance of electrical conductivity. Ishihara et al. [1995] reported that electrical conductivity of the perovskite system $LaGaO_3$ decreased with doping of rare earth cation for La- site in the following order, $Nd^{3+} > Sm^{3+} > Gd^{3+} > Yb^{3+} > Y^{3+}$ respectively. The electrical conductivity of Sr^{2+} doped of $LaMnO_3$ system reveals that conductivity increases with increasing weight percentage of dopant [Kamata et al. (1995)]. In $Gd_{1-x}A_xCo_{1-y}Mn_yO_3$ ($A=Sr, Ca; y=0-1.0$) system, low level compositions of Co have shown good electrical conductivity and also got better electrochemical behaviour as compare to pure magnate [Phillipps et al. (1999)]. Li et al. [2010] have investigated that the ionic conductivity of La^{3+} doped $SrTiO_3$ system increased but the electronic conductivity decreased with increasing A-site deficiency level. The electrical conductivity of $La_{0.8}Sr_{0.2}GaO_3$ system was increased with doping of Fe, Co, or Ni at Ga site respectively as a function of temperature [Ishihara et al. (2000)]. Bukhari et al.[2009] observed that Ce^{3+} substituted $SmFeO_3$ system, achieved higher conductivity in reducing than in oxidizing atmosphere which concluded that doping at the A-site has transformed the conducting behaviour of $SmFeO_3$ from p-type to n-type. $PrCO_3$, $LaFeO_3$, $LaMnO_3$ and $LaCoO_3$ systems have been found to show increased electrical conductivity with doping of various alkaline earth ions at A- site [Anderson et al. (1992)]. The electrical conductivity of doped double perovskite Sr_2MgMoO_6 system was found to decrease with doping of W and Nb [Vasala et al. (2010)]. Xie et. al. [2011] studied and found that the electrical conductivity of Al^{3+} doped $Sr_2MgMoO_{6-\delta}$ (SMMO) is strongly dependent on the preparing environment and prepared samples reduced in 5% H_2/Ar that exhibited higher conductivity than those in unreduced environment. Various doping of isovalent and aliovalent substitution affects the electrical conductivity of perovskite and double perovskite anode materials. It was observed that Ca^{2+} doped $LaCrO_3$ decreases the electrical conductivity with increasing of Ca^{2+} concentration which occurs due to neutralization of number of small

polarons attributed to formation of oxygen vacancies with increase in Ca^{2+} content [Mukherjee et al. (2012)]. Sr doped LaMnO_3 system depicted that electronic conductivity increases with increasing of dopants content (up to 1000 °C) in oxygen partial pressure [Mizusaki et al. (2000)]. Tao et al.[2003] also reported the electrical conductivity of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ which was measured as a function of $p\text{O}_2$ at 900 °C. For this system, conductivity retains a constant value at $\sim 38 \text{ S cm}^{-1}$ $p\text{O}_2$ above 10^{-10} atm; but at lower $p\text{O}_2$, conductivity decreases indicating p-type conductivity due to dominant electronic mechanism. The electrical conductivity of lanthanum and yttrium doped SrTiO_3 system was found to show the highest conductivity $\sim 100 \text{ Scm}^{-1}$ at 800 °C [Hui et al. (2002)]. Blennvo et al. [2009] have also reported that conductivity of SrTiO_3 increases up to $\sim 120 \text{ Scm}^{-1}$ with doping of Nb at Ti sites. The aliovalent (Nb) doping on $\text{Sr}_2\text{MgMoO}_{6-\delta}$ system decreases the electrical conductivity with increasing dopant content and decrease with isovalent (W) doping which is occurred due to increase of oxygen-vacancy concentration [Vasala et al. (2010)]. Xie et al. [2011] reported that electrical conductivity of $\text{Sr}_2\text{MgMoO}_{6-\delta}$ increases with increase of Al doping up to 5 weight % with the unreduced optimum value of $\sim 5.4 \text{ Scm}^{-1}$ at 800 °C. This is due to generation of oxygen vacancy and with reduction of Mo^{6+} to Mo^{5+} under reducing atmosphere. La-doped (6 weight %) $\text{Sr}_2\text{MgMoO}_6$ has been resulted the electrical conductivity $\sim 7.5 \text{ Scm}^{-1}$ at 800 °C in dry CH_4 [Xie et al. (2011)]. Zhang et al. [198] observed that the electrical conductivity of Sm^{3+} doped $\text{Sr}_2\text{MgMoO}_6$ system is increased with the substitution of Sm^{3+} for Sr^{2+} and 6 weight % doping get higher value ($\sim 16 \text{ Scm}^{-1}$) in H_2 at 800 °C. In the above studied system, electronic conduction is observed through an electron hopping conduction mechanism between Mo^{6+} and Mo^{5+} . He et al. [199] reported that the electrical conductivity of Ti doped $\text{Sr}_2\text{NiMoO}_6$ is resulted $\sim 17.5 \text{ Scm}^{-1}$ at 800 °C for composition $x = 0.5$ which is associated with electron delocalization and covalent nature of the $-\text{Mo}^{6+}-\text{O}-\text{Ti}$ (Ni) $-\text{O}-\text{Mo}^{5+}$ bond. With substitution of Ni in $\text{Sr}_2\text{MgMoO}_6$ system, electrical conductivity increases with increasing Ni content because of the increase in the concentration of electronic defects, $[\text{Mo}_{\text{Mo}^{6+}}^{5+}]$, and the decreased band gap energy [Xie et al. (2014)]. Neagu et al. [2011] observed that δ and σ both were increased significantly with Ga doping in $\text{La}_{0.4}\text{Sr}_{0.4}\text{Ti}_{1-x}\text{O}_{3-x/2-\delta}$ system. The electrical conductivity for above system also increased with doping at maximum $\sigma \sim 50 \text{ Scm}^{-1}$ (operating temperature at 880 °C in 5% H_2/Ar on ~ 62 % dense pellet) for composition $x = 0.05$.

1.8 Processing of Rare Earth Doped Perovskite (LaCrO₃) and Double Perovskite (Sr₂NiMoO₆) Systems

The main objective of the present study is to investigate the correlation of the structural and electrical conductivity of rare earth doped perovskite (LaCrO₃) and double perovskite (Sr₂NiMoO₆) materials for SOFC. Various techniques have been developed to synthesize the LaCrO₃ and Sr₂NiMoO₆ powders. Few of them are solid state ceramic route, [Prasatkhetragarn et al. (2009) and Bansal et al. (1981)] urea based homogeneous precipitation [Silva et al. (2009)], sol-gel [Wei et al. (2008)], Nitrate solutions method [Filonova et al. (2013)], microwave-assisted combustion method [Xiao et al. (2011)], a wet-chemical route [Vasala et al. (2010)], auto-combustion (Auto ignition) process [Xiao et al. (2014)] nitrate-citrate combustion method etc. [Xie et al. (2014)]. These techniques were found their individual merits and demerits. For solid state ceramic route high sintering temperature (~1500 °C) is needed for densification that is not economical [Hakuta et al. (1998)]. Hydrothermal method requires long term heat treatment for long duration because of the slow reaction rate [Seo et al. (2006), Chung & Lee (2004) and Kingsly et al. (1990)]. Among the accessible wet chemical route, combustion technique is suitable for producing ultra fine powders of oxide ceramics in shorter time duration and at low temperature makes excellence of powder characteristics [Ferreira et al. (1992) and Kingsley (1988)]. The achievement of this process is an intimate blending among the constituents via suitable fuel or complexing agents (e.g. citric acid, urea and glycin) in an aqueous medium followed by an exothermic redox reaction between fuel and oxidizer (i.e. Nitrates) [Chavan and Tyagi, (2004)]. Once initiated auto-ignition process, it remains self-sustain to continue the combustion of precursors. The large volume of gases during synthesis process is evaluated. The combustion dissipates the heat of ignition and limits the increasing temperature, thus reducing the possibility of temperature limited partial sintering among the primary particle. Among the given emphasis of these techniques citrate-nitrate auto-combustion route is relatively simple and low-cost process to synthesize ceramic powder oxides.

1.9 The Main Objective of Present Investigation

In order to contribution in the development of anode materials for SOFCs, the prime objectives of the present research work is as follows:

- To synthesize a few series of rare earth (Gd^{3+}) doped perovskite ($LaCrO_3$) and (La^{3+} , Ce^{3+} , and Sm^{3+}) doped double perovskite (Sr_2NiMoO_6) anode materials by chemical reaction routes.
- To study the thermal behavior of the as prepared and sintered samples using differential scanning calorimetry (DSC) and thermogravimetry (TG), analysis.
- To study the phase formation and crystal structure of the prepared anode materials using powder X-ray diffraction technique.
- To determine the density and porosity of sintered samples using Archimedes' principle.
- To study effect of doping on temperature dependence conductivity behavior of prepared samples using complex plane impedance spectroscopy.
- To study the microstructure employing scanning electron microscopy (SEM) and its correlation to the conduction mechanism.
- To study the oxidation state of the ions and oxygen vacancies by X-ray photoelectron spectroscopy (XPS) and its effect on the conduction mechanism.
- To investigate temperature dependent electrical conductivity of a few promising candidate in reducing atmosphere.
- To study the thermal expansion coefficient (TEC) using dilatometer to check thermal compatibility with the investigated electrolytes.