

SYNTHESIS AND CHARACTERIZATION OF
 $\text{La}_{1-x}\text{M}_x\text{TO}_y$ AND $\text{Y}_{1-x}\text{M}_x\text{TO}_y$ (M=Ca, Sr; T=Ti, Nb)
MATERIALS FOR SOLID OXIDE FUEL CELLS

A

Thesis

Submitted for the award of the degree of

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BY

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**DEDICATED TO MY LOVING
SISTER**

CERTIFICATE

This is to certify that the thesis entitled "**Synthesis and Characterization of $\text{La}_{1-x}\text{M}_x\text{TO}_y$ and $\text{Y}_{1-x}\text{M}_x\text{TO}_y$ ($\text{M}=\text{Ca}, \text{Sr}$; $\text{T}=\text{Ti}, \text{Nb}$) materials for solid oxide fuel cells**" which is being submitted by Ms. Jasmeet Kaur Gill to School of Physics and Materials Science, Thapar University, Patiala in fulfilment of the requirements for the award of the degree of Doctor of Philosophy, is a record of candidate's own work carried out by her under our guidance and supervision. The matter presented in this thesis has not been submitted in part or full for the award of any degree in any other University or Institute.

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PREFACE

The significant progress in the research and development of solid oxide fuel cells (SOFCs) has lead them to achieve the ultimate goal of commercialization. Solid oxide fuel cells are the most efficient devices for conversion of chemical fuels directly into electrical power. All over the world, lot of research is being carried out to search new electrolyte materials which have good thermal, structural stability in working atmosphere of SOFCs.

Pyrochlore compounds ($A_2B_2O_7$) can be used as solid electrolyte in solid oxide fuel cell. These compounds show order and disorder transition due to disordering in cations and /or anions. The magnitude of this disordering depends on the ionic radii difference between cations at the A and B sites. Interchangeability of A and B cations enhances the formation of anion Frankel defects which leads to good ionic conductivity in these systems. Basically, pyrochlore compounds are inherent ionic conductors whose properties may be altered by changing the processing conditions and doping of different elements on various sites. Yttrium titanate, $Y_2Ti_2O_7$, is an important member of the pyrochlore family because it exhibits various properties which make it suitable for potential applications in different fields. Yttrium titanate ($Y_2Ti_2O_7$) exhibits n-type conductivity at lower partial pressure of oxygen (p_{O_2}) while oxide ion conductivity was observed at high oxygen pressure. In the present work, it has been planned to investigate the effect of systematic doping of SrO, CaO for Y_2O_3 as well as La_2O_3 in $Y_2Ti_2O_7$ and $La_2Ti_2O_7$ system. Different concentration of Sr^{2+} and Ca^{2+} doping was chosen to find the solid solubility limit and its affect on conductivity. The results are discussed in light of oxygen vacancies, order and disorder transitions using electrical conductivity, X-ray analysis, Fourier Transform-Infrared Spectroscopy, thermal expansion coefficient (TEC) and scanning electron microscope (SEM) in-order to check their suitability for Solid Oxide Fuel Cells (SOFC).

Moreover, LaNbO_4 system has also been studied by many research groups to check its applicability and suitability as a potential electrolyte candidate for SOFC. LaNbO_4 based materials are stable in $\text{CO}_2/\text{H}_2\text{O}$ atmosphere and exhibits conductivity nearly 10^{-3} Scm^{-1} . It was observed that partial substitution of La by Ce, Pr and Nb by Mn, W, Cr in LaNbO_4 system exhibited good electronic conductivity. The maximum value of conductivity reported for acceptor doped LaNbO_4 system is of $8 \times 10^{-4} \text{ Scm}^{-1}$ at 900°C in wet hydrogen. Recently, acceptor doped $(\text{Ca}, \text{Sr})\text{LaNbO}_4$ system which are stable in operating atmospheres have been reported as candidates for proton conducting electrolytes and these materials were hence, chosen for the present studies. The effect of acceptor doping (Sr, Ca) on A-site of ABO_4 ($\text{A}=\text{La}, \text{Y}$) materials were further investigated. The entire work in this thesis is presented in five chapters.

Chapter 1 deals with background and fundamentals of solid oxide fuel cell and their components. These are described in first section of the chapter. The various electrolyte materials exhibiting fluorite, perovskite and pyrochlore based structures are discussed in detail. The mechanism of ion conductivity which is the key feature of the solid electrolytes is given. Further, effect of doping on electrical conductivity is explained in detail. In addition to this, a comparison between electrolytes based on proton conducting materials and oxide ion conductors have been investigated. Moreover, applications of solid electrolytes in different areas are also presented.

Chapter 2 gives a detailed account of the literature survey in context of pyrochlore systems. Since doping plays an important role in case of titanate pyrochlores $\text{A}_2\text{Ti}_2\text{O}_7$ ($\text{A}=\text{Y}$), the role of dopants on the properties of pyrochlore structure is described in first section of the chapter. The electrical, thermoelectric, optical, structural properties and thermal conductivity of $\text{Y}_2\text{Ti}_2\text{O}_7$ have

been investigated extensively by various researchers. Perovskite materials have also been the subject of great deal of research for SOFC electrolyte applications. In addition to oxide ion conducting materials, proton conducting oxides are also discussed as electrolytes in fuel cells.

Chapter 3 describes about experimental procedure followed in the present work. On the basis of literature survey, $\text{La}_{1-x}\text{M}_x\text{TiO}_y$ and $\text{Y}_{1-x}\text{M}_x\text{TiO}_y$ ($\text{M}=\text{Ca}, \text{Sr}$; $\text{T}=\text{Ti}, \text{Nb}$) system with $x=0, 0.1, 0.2, 0.3, 0.4$ were synthesized by solid state reaction method at different sintering temperature and processing conditions. The as prepared samples were characterized by different characterization techniques. In addition to this, the interaction study of two systems $\text{Y}_2\text{Ti}_2\text{O}_7$ (electrolyte) and $40\text{SiO}_2.30\text{BaO}.20\text{ZnO}.10\text{Y}_2\text{O}_3$ based glasses have been done for study of chemical interactions between them to understand the kinetics of the formation of different crystalline phases with respect to the heat treatment temperature and duration.

Chapter 4 deals with results and discussions of as prepared samples. The chapter is divided in *five sections*; in the *first section* the effect of systematic doping of Sr^{2+} and Ca^{2+} for Y^{3+} in $\text{Y}_{1-x}\text{M}_x\text{TiO}_y$ ($\text{M}=\text{Ca}, \text{Sr}$) system with $x=0, 0.1, 0.2, 0.3, 0.4$ was chosen to find the solid solubility limit and its affect on conductivity. The results are discussed in light of oxygen vacancies, order and disorder transitions using electrical conductivity, X-ray analysis, FTIR, TGA, TEC and SEM in-order to check its suitability for solid oxide fuel cells (SOFC). *Second, third and fourth sections* comprises of the effect of systematic doping of Sr^{2+} and Ca^{2+} for La^{3+} in $\text{La}_{1-x}\text{M}_x\text{NbO}_y$ ($\text{M}=\text{Ca}, \text{Sr}$) system, Y^{3+} in $\text{Y}_{1-x}\text{M}_x\text{NbO}_y$ ($\text{M}=\text{Ca}, \text{Sr}$) system, La^{3+} in $\text{La}_{1-x}\text{M}_x\text{TiO}_y$ ($\text{M}=\text{Ca}, \text{Sr}$) system with $x=0, 0.1, 0.2, 0.3, 0.4$ respectively. *Fifth section* comprises of the chemical interaction study between candidate glass sealant ($40\text{SiO}_2.30\text{BaO}.20\text{ZnO}.10\text{Y}_2\text{O}_3$) and Ca^{2+}

doped $\text{Y}_2\text{Ti}_2\text{O}_7$ system. The selection of Ca^{2+} doped pyrochlore is based on its better thermal stability and presence of Y_2O_3 in both the samples of glass sealant and electrolyte. The purpose of this study was to understand the kinetics of the formation of different crystalline phases with respect to the heat treatment temperature and duration.

Chapter 5 summarizes the results of all the experiments conducted for the doping of Sr^{2+} and Ca^{2+} viz $\text{Y}_{1-x}\text{M}_x\text{TiO}_y$, $\text{La}_{1-x}\text{M}_x\text{NbO}_y$, $\text{Y}_{1-x}\text{M}_x\text{NbO}_y$, $\text{La}_{1-x}\text{M}_x\text{TiO}_y$ ($x=0, 0.1, 0.2, 0.3, 0.4$) systems. The overall conclusion shows that doping of Sr^{2+} and Ca^{2+} plays very crucial role to increase the disordering as well as oxygen vacancies leading to increase in conductivity values of $\text{Y}_2\text{Ti}_2\text{O}_7$ system. On the other hand, it is found that higher doping concentration leads to secondary phase formation which inhibits the grain growth that ultimately reduces density with increase in porosity. Moreover, it is observed that effect of Ca^{2+} doping in $\text{Y}_2\text{Ti}_2\text{O}_7$ system is more effective than Sr^{2+} doping in $\text{Y}_2\text{Ti}_2\text{O}_7$ system due to occurrence of higher disordering leading to decrease in density with increase in porosity.

On the other hand, XRD patterns of Sr^{2+} and Ca^{2+} doped LaNbO_4 samples indicate the formation of secondary phase with its increasing volume fraction. It is observed that $\text{La}_{0.95}\text{Sr}_{0.05}\text{NbO}_4$ phase is more conducting than LaNbO_4 phase. A major conductivity difference observed in $\text{La}_{1-x}\text{M}_x\text{NbO}_y$ system with $x=0.4$ i.e., $1.01 \times 10^{-1} \text{ Scm}^{-1}$ shows that this sample exhibits higher vacancies which provide path for ion conduction. The UV visible results also show the drastic change in band gap of this particular sample $\sim 2.6 \text{ eV}$. In addition to above system, the effect of systematic doping of SrO and CaO for Y_2O_3 in YNbO_4 system was also studied. It was observed that the undoped sample exhibit single phase i.e., YNbO_4 . The doping of Sr^{2+} in present system

leads to secondary phase formation such as $\text{Sr}_2\text{Nb}_2\text{O}_7$ and SrNb_2O_6 . The formed secondary phases enhance the electrical conductivity by five orders of magnitude.

The interaction study between $(\text{Y}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_{7-x}$ for $x=0.1$ and $40\text{SiO}_2.30\text{BaO}.20\text{ZnO}.10\text{Y}_2\text{O}_3$ glass results in formation of different crystalline phases such as $\text{Y}_2\text{Ti}_2\text{O}_7$, $\text{BaZn}(\text{SiO}_4)$, $\text{Ca}(\text{SiO}_3)$ and SiO_2 . It is observed that the volume fraction of detrimental phase (SiO_2) decreases with increase in duration of heat treatment of 100h. The overall interaction study indicate that the above system can be a good substitute for long hour operation of SOFC as compared to the existing one as there is no crack observed in the system though porosity exists. The TEC values are also of same order as required for SOFC. The suggestion for future scope is also given.

At the end, the list of papers published, presented and communicated are also appended.

APPENDIX

Shannon Ionic Radii of various cations

Cations	Ionic radii (Å)	Coordination number
Y³⁺	1.02	8
Sr²⁺	1.26	8
Ca²⁺	1.12	8
La³⁺	1.16	8
Ti³⁺	0.67	6
Ti⁴⁺	0.61	6
Nb³⁺	0.72	6
Nb⁴⁺	0.68	6
Nb⁵⁺	0.64	6

INTRODUCTION

Overview

This chapter deals with fuel cells and emphasis on varieties of solid electrolytes used in solid oxide fuel cell (SOFC). The electrolyte is a major component of an electrochemical cell and should have sufficiently high ionic with low electronic conductivity at the cell operating temperature. The various electrolyte materials exhibiting fluorite, perovskite and pyrochlore based structures are discussed in detail. It is observed that in case of pyrochlore structure, the interchangeability of A and B cations enhances the formation of anion Frankel defects which lead to the good ionic conductivity in these systems. The mechanism of ion conductivity which is the key feature of the solid electrolytes is given. Further, effect of doping on electrical conductivity is explained in detail. In addition to this, a comparison between electrolytes based on proton conducting materials and oxide ion conductors have been investigated. Solid electrolytes for solid oxide fuel cell and their fabrication techniques are also discussed along with other aspects concerning solid oxide fuel cell. Moreover, applications of solid electrolytes in different areas are also presented.

1.1 Fuel cells

All over the world research is going on to search for clean and efficient energy source. One approach to meet this challenge is through fuel cells. The basic principle of fuel cells is based on the conversion of gaseous fuels (hydrogen, natural gas, gasified coal) via an electrochemical reaction directly into electricity. The high energy conversion efficiency is an important feature of a fuel cell. This is due to the fact that a fuel cell converts the chemical energy of the fuel directly to electrical energy. A fuel cell unlike battery does not need to be charged. It can produce continuous power when fuel is supplied to it [1, 2]. For it varieties of fuel cells have been developed. However, each fuel cell differs in materials of construction, fabrication techniques and the system requirements, in addition to their classification on the basis of the type of electrolyte used. Currently, different types of fuel cells are under development:

- Low temperature fuel cells (room temperature to 90 °C) such as Solid Polymer Electrolyte Fuel Cell (PEMFC) and the Alkaline Fuel Cell (AFC).
- A medium temperature fuel cell (160-220 °C) such as Phosphoric Acid Fuel Cell (PAFC) classified as first generation fuel cell.
- A high temperature fuel cell operating around 650 °C i.e., Molten Carbonate Fuel Cell (MCFC) classified as second generation fuel cell.
- Third generation fuel cell or Solid Oxide Fuel Cell (SOFC) which operates at temperature around 800-1000 °C.

As shown in figure 1.1, in alkaline fuel cell (AFC), polymeric-electrolyte-membrane fuel cell (PEMFC) and phosphoric-acid fuel cell (PAFC) pure hydrogen is supplied to the anode. However, hydrocarbon or alcohol fuels require an external fuel processor to be incorporated in the system [3]. This increases the cost as well as complexity of the system. On the other hand, in case of molten-

carbonate fuel cells (MCFCs) and solid oxide fuel cells (SOFCs) both CO, H₂ electrochemically oxidizes at the anode since they operate at much higher temperature than other fuel cells.

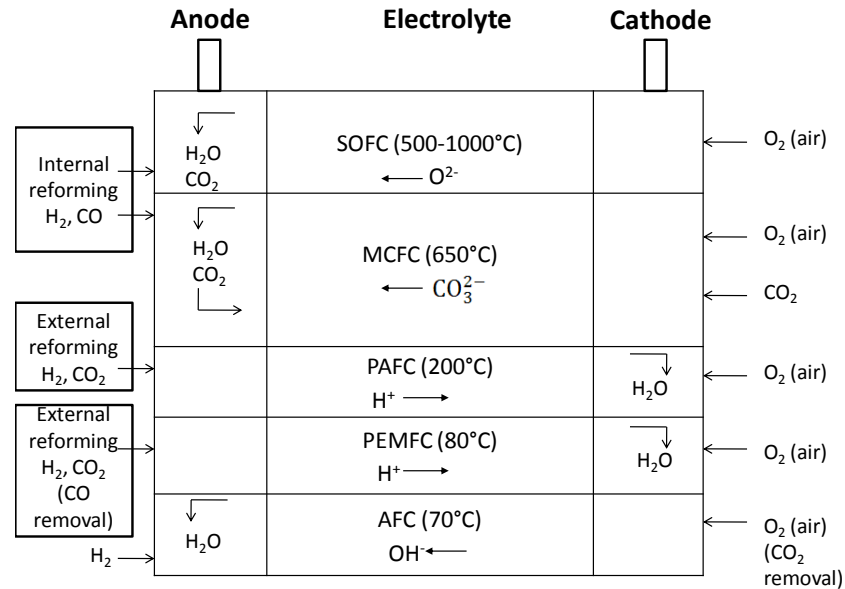


Figure 1.1: Comparison of various types of fuel cells and their reaction products at anode, cathode and electrolyte components [3].

Table 1.1: Comparison of features of various types of fuel cells [4].

Type	Temperature (°C)	Fuel	Electrolyte	Mobile ion
PEM: polymer electrolyte membrane	70–110	H ₂ , CH ₃ OH	Sulfonated polymers (Nafion)	(H ₂ O) _n H ⁺
AFC: alkali fuel cell	100–250	H ₂	Aqueous KOH	OH ⁻
PAFC: phosphoric acid fuel cell	150–250	H ₂	H ₃ PO ₄	H ⁺
MCFC: molten carbonate fuel cell	500–700	hydrocarbons, CO	(Na,K) ₂ CO ₃	CO ₃ ²⁻
SOFC: solid oxide fuel cell	700–1000	hydrocarbons, CO	(Zr,Y)O _{2-δ}	O ²⁻

1.2 Solid oxide fuel cells (SOFC)

The significant progress in the research and development of solid oxide fuel cells (SOFCs) has led them to achieve the ultimate goal of commercialization. SOFCs are the most efficient devices for conversion of chemical fuels directly into electrical power. Considerable advances in theory and experiments are still being made over after 100 years of invention of its basic idea and materials by Nernst and his colleagues. On the molecular scale, collisions between hydrogen and oxygen molecules result in a reaction producing water and releasing heat whereas the bond energy of the produced water is lower than the bonding configuration of the initial hydrogen and oxygen gases. This energy difference is released as heat for combustion engines which occur by reconfiguration of electrons in picoseconds at an intimate, subatomic scale. To produce electricity, this heat energy must be converted into mechanical energy and then the mechanical energy must be converted into electrical energy which is potentially complex and inefficient.

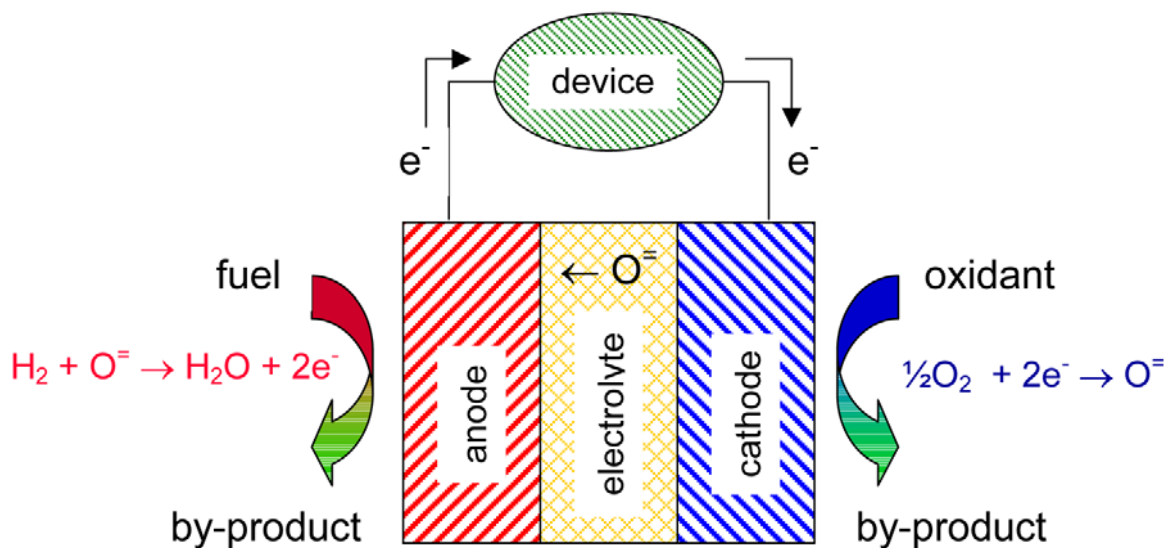


Figure 1.2: Working of solid oxide fuel cell [4].

SOFC consists of the two porous electrodes (anode and cathode) separated by a dense, ionic-conducting solid electrolyte. Oxygen ions, created by surface reactions in the cathode, migrate from

cathode to anode through the electrolyte and combine with fuel. The overall reaction produces water and free electrons as indicated in figure 1.2. A single unit of SOFC can produce only one volt output. In order, to produce higher voltage, SOFC units are stacked on each other and are connected by interconnect. The operational cell voltage is always smaller than the ideal cell voltage due to presence of activation polarization, concentration polarization and ohmic polarization [5]. The activation polarization arises from the slow electrochemical reaction kinetics. The concentration polarization is associated with the diffusion of source and product gases. The activation polarization loss is dominant at low current density and concentration polarization occurs over an entire range of current density. On the other hand, ohmic polarization is due to the resistance to the flow of ions in the electrolyte as well as resistance to the flow of electrons in the electrodes. In addition to this, SOFC offers a clean, pollution-free way to generate electricity at efficiencies higher than other types of fuel cells. Since SOFC unit comprises of several components and performance of each component plays important role to extract electricity from the units; it is essential to develop and evaluate the required properties of these components. All over the world, lot of research is being carried out to search new materials which have the good thermal, structural stability in working atmosphere of SOFCs. There has been a commercial, cost-effective application of the SOFC technology for power generation for different applications [6].

- ❖ At low power level, around 1-10 W, small SOFC devices are used as battery replacements on remote sites due to high cost of recharging or replacement of batteries in comparison to fuel for fuel cells.
- ❖ At some higher power level i.e., 100W to 1kW they are used for military applications which require lightweight portable power sources to be carried by troops for communication and weapon power.

- ❖ At 1-10 kW level, SOFC systems provide supply power to residential buildings and auxiliary power units in vehicles and trucks.
- ❖ At 10kW to a few MW, SOFCs systems are used in place of diesel engines due to their reliability and low maintenance.
- ❖ Above 1MW range, SOFC systems can be used with turbine power plants to increase efficiency and reduce pollutants emissions.

Many companies are involved in developing and testing of SOFC systems such as Siemens Westinghouse Power Corporation, Sulzer Hexis . On the other hand, high cost of SOFC system is the major obstacle in the path of commercialization of SOFC.

1.3 Intermediate temperature solid oxide fuel cell (ITSOFC)

In order to achieve sufficiently high ionic conductivity and high efficiency, SOFCs are operated at high temperature around 1000 °C. On the other hand, the high temperature operation of SOFC causes many problems such as mechanical stresses due to difference in thermal expansion of components, interfacial diffusion across the electrolyte and electrodes and thus results in imposing severe restriction on the choice of materials. In order to overcome these problems, intermediate temperature solid oxide fuel cell (ITSOFC) operating at 600-800 °C is being developed. The basic requirements to develop ITSOFC consists of use of thin electrolyte membrane to minimize the ohmic loss of electrolyte and to develop new electrolyte materials which exhibit high oxide ion conductivity at reduced temperature [7]. In addition to above, research efforts are being focused on the development of intermediate to low temperature (400-700 °C) SOFCs [8].

1.4 Cell configuration

SOFC consists of mainly two kinds of the cell configurations which are described below.

1.4.1 Tubular cell

The schematic view of tubular cell is shown in figure 1.3. In this, the electrolyte and electrode layers are grown on a porous zirconia or LaMnO_3 tube. The interconnect is fabricated to touch the cathode layer and the cells are connected in series by pushing the interconnect on the surface of anode of the neighbor cell by using a nickel felt. Fuel gas is supplied from the bottom. After being consumed for the electrochemical reaction, the unreacted gas is burned for pre-heating of air which is supplied from the top of alumina tube inside the cell. With this design, gas sealing material is not required [9]. The main demerit of this design is the long electronic path per cell. The generated electricity should go through the electrode layer to reach to the next cell. Since the electrode is porous, so the electrical conductivity is not too high. In addition to this, another type of tubular SOFC is also developed where multiple cells are mounted on one tube where the problem of low electronic conductivity is also experienced by this type of cell. Additionally, high cost is involved in the development of SOFC components due to sophistication of the deposition techniques.

1.4.2 Planar cell

The planar cell configuration consists of flat anode/electrolyte/cathode layers which are stacked on top of each other. The planar cell configuration has an advantage over the tubular cell in terms of electrical path where higher power density is obtained. However, some technological problems are observed in making planar SOFC such as difficulty in gas sealing, fragility of electrolyte and interconnect (separator).

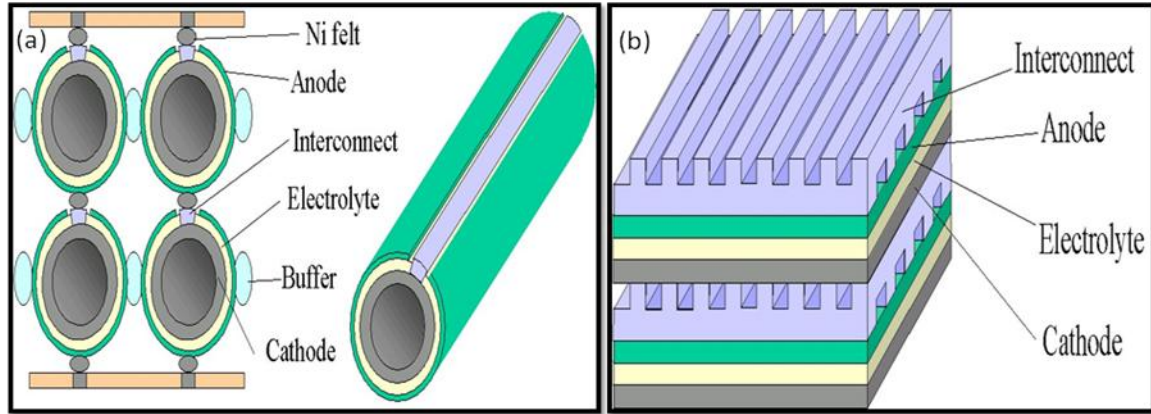


Figure 1.3: (a) Schematic of the tubular cell and (b) typical planar-type cell.

1.5 Components of SOFC

The principle components of SOFC are the electrolyte, the anode, the cathode and the interconnect. Each component serves several functions in SOFC and must meet certain requirements. The materials commonly used for SOFC are nickel/ stabilized zirconia cermet for anodes, doped lanthanum manganite for cathodes, doped lanthanum chromite for interconnects and yttria stabilized zirconia for electrolyte. The major component of an electrochemical cell is the electrolyte, which is ionically conducting membrane that separates the two electrodes.

1.6 Properties of electrolyte materials

Fuel cell efficiency depends on the properties of materials from which the cell is fabricated. One of the most critical components in the fuel cell is the solid electrolyte.

Solid electrolytes should satisfy number of requirements such as [10]:

- ❖ The electrolyte must be stable in both reducing and oxidizing environments.
- ❖ It must have sufficiently high ionic conductivity ($\geq 0.1 \text{ Scm}^{-1}$ at 900°C) with low electronic conductivity at the cell operating temperature.
- ❖ Low electronic transference number ($< 10^{-3}$ at 900°C) and phase stability in wide range of

temperature (RT - 900°C).

- ❖ Thermodynamic stability over a wide range of temperature and oxygen partial pressure.
- ❖ They must have thermal expansion characteristics compatible with other components such as electrodes.
- ❖ Phase stability from room temperature to 1100°C.
- ❖ Negligible volatilization of components and no gas leakage.
- ❖ Mechanical stability and chemical compatibility with electrodes, sealants and interconnect materials in oxidizing and reducing atmosphere.
- ❖ Negligible interaction with electrode materials under operation condition.
- ❖ Fracture toughness (>400 MPa at room temperature) and moderate cost of materials and easy fabrication.

1.7 Electrolyte materials for SOFC

Much of the research is focused for optimization of the structure to achieve high ionic conductivity of the solid electrolyte. Until now, stabilized zirconia, especially yttria-stabilized zirconia, possessing the fluorite structure, has been the most favored electrolyte for SOFCs. Moreover, doped ZrO_2 , CeO_2 and Bi_2O_3 are considered as candidate electrolyte materials for ceramic oxygen generators and solid oxide fuel cell (SOFC) [11-14]. Among these, the electrolyte materials derived from bismuth oxide (Bi_2O_3) compositions show the highest conductivity as compared to others, particularly below 600°C [15, 16]. More recently, several other materials, including perovskites and pyrochlore structured oxides, have also been found to possess good ionic conductivity. Various electrolyte materials which are currently in use as a solid electrolyte in different devices are discussed below:

1.8 Fluorite structured electrolytes

The fluorite structure is a face-centered cubic arrangement of cations with anions occupying all the tetrahedral sites, leading to a large number of octahedral interstitial voids. Oxide ion conductivity was first observed in ZrO_2 containing 15 wt% Y_2O_3 (yttria-stabilised zirconia or YSZ) by Nernst [17] in the 1890s. In 1937, Baur and Preis [18] constructed the first SOFC using this electrolyte. At high temperatures, zirconia has the fluorite structure, stabilized by addition of divalent or trivalent (i.e. aliovalent) cations such as Ca or Y at lower temperatures. Pure ceria also has the fluorite structure. Oxide ion conduction is provided by oxide ion vacancies and interstitial oxide ions.

1.8.1 Stabilized zirconia as oxide-ion conductors

Yttria stabilized zirconia is the most common electrolyte material for SOFCs. The material possesses good oxygen-ion conductivity and exhibits stability in both oxidizing and reducing atmospheres. Undoped ZrO_2 does not serve as a good electrolyte material due to its low ionic conductivity. At the room temperature, ZrO_2 has a monoclinic crystal structure. The monoclinic structure changes to tetragonal form above 1170°C and to a cubic fluorite structure above 2370°C [10]. However, the addition of certain aliovalent oxides stabilizes the cubic fluorite structure of ZrO_2 from room temperature to its melting point and increases oxygen vacancy concentration. The most commonly used dopants are CaO, MgO, Y_2O_3 , Sc_2O_3 and certain rare earth oxides. These oxides exhibit high solubility in ZrO_2 and are able to form the fluorite structure which is stable over wide range of composition and temperature.

Table 1.2: Conductivity data for stabilized ZrO₂ doped with rare-earth oxides [19].

Dopant (M ₂ O ₃)	Composition (mol% M ₂ O ₃)	Conductivity (1000°C) (x10 ⁻² S cm ⁻¹)	Activation energy (kJ mol ⁻¹)
Y ₂ O ₃	8	10.0	96
Nd ₂ O ₃	15	1.4	104
Sm ₂ O ₃	10	5.8	92
Yb ₂ O ₃	10	11.0	82
Sc ₂ O ₃	10	25.0	62

1.8.2 Doped CeO₂ as oxide-ion conductors

Ceria oxide exhibits the crystal structure of zirconia (cubic fluorite). Undoped CeO₂ is a poor oxide ion conductor. However, the ionic conductivity of CeO₂ can be improved significantly by creating oxygen vacancies if the substitution of the Ce⁴⁺ ion with some trivalent oxides are done [20]. Doped CeO₂ exhibit higher conductivity than YSZ (Ytria stabilized zirconia) or ScSZ (Scandium stabilized zirconia) at low temperature. Thus doped ceria has been considered as a possible solid electrolyte for intermediate temperature SOFCs. Ceria is doped to increase the concentration of oxygen vacancies leading to increase in ionic conductivity. The most common dopants used for ceria are gadolinium, cerium and samarium [21]. Moreover, Ceria (CeO₂) doped with CaO, Y₂O₃ and various rare-earth oxides shows higher conductivity, lower activation energy in comparison to stabilized ZrO₂ [22]. Further, doping of zinc oxide on yttria doped ceria (YDC) was done in order to increase the density as well as ionic conductivity of the materials [23]. In addition to this, neodymium-doped ceria (NDC) powders of nano dimensions helps to increase the ionic conductivity of NDC powders with minimum activation energy [20]. However, the main drawback

of this material is that they need to be sintered at very high temperatures, between 1500 °C and 1600 °C, in order to achieve good density. Apart from this, the reduction of Ce^{4+} to Ce^{3+} occurs under the SOFC anode reducing atmosphere with increase in electronic conductivity [24]. In other words, the material exhibits electronic conductivity and large departure from stoichiometry at elevated temperatures in a reducing atmosphere. In addition to this, the primary challenge is stability of these electrolytes at low oxygen partial pressure [7, 25]. Gadolinium-calcia-doped ceria ceramics has shown to improve total ionic conductivity as well as helps in inhibiting the redox reaction Ce^{4+} to Ce^{3+} [26]. Further, ceria-based composites i.e., GDC/(Li_2CO_3 - K_2CO_3) (70/30 wt %) have been developed and found to exhibit good thermal stability with good ionic conductivity. These composite materials can be considered to be used as potential electrolytes for IT SOFC [27].

Table 1.3: Electrical conductivity data for $\text{CeO}_2\text{-Ln}_2\text{O}_3$.

Electrolyte	Conductivity (Scm^{-1})		Activation energy (kJmol^{-1})	References
	500 °C	700 °C		
CeO_2 -10 mol% Sm_2O_3	5.0×10^{-3}	4.0×10^{-2}	75	28
CeO_2 -10 mol% Gd_2O_3	3.8×10^{-3}	3.6×10^{-2}	70	29
CeO_2 -10 mol% Y_2O_3	0.21×10^{-3}	1.0×10^{-2}	95	28
CeO_2 -10 mol% CaO	1.5×10^{-3}	2.0×10^{-2}	80	29

1.8.3 Stabilized bismuth oxide (Bi_2O_3) as oxide-ion conductors

Electrolyte material such as doped bismuth oxide exhibit superior ionic conductivity over YSZ and CeO_2 based electrolytes at lower temperature [28]. Structurally, higher disorder state is responsible for high ionic conductivity in Bi_2O_3 systems. Bi_2O_3 exhibits four polymorphs viz. α , β , γ and δ . The conductivity of various phases [29] is given in table 1.4. Takahashi et al., [30] reported enhancement of ionic conductivity over a factor of 3 due to the oxygen ion movement during

transition of low temperature α to high temperature δ -phase. Stabilized bismuth oxides (Bi_2O_3) exhibits the ionic conductivity of 10^{-1} Scm^{-1} at 700°C and 10^{-1} Scm^{-1} at 500°C which makes this material suitable to be used as electrolyte material for SOFC. The main drawback of this material is its smaller oxygen partial pressure range of ionic conduction, thermodynamic instability in reducing atmosphere and low mechanical strength [10]. Stabilized Bi_2O_3 is easily reduced under low oxygen partial pressure and decomposes into bismuth metal at oxygen partial pressure of about 10^{-13} atm at 600°C [31].

Table 1.4: Conductivity of the various phases of Bi_2O_3 .

Phase	Conductivity at 650°C (Scm^{-1})
$\alpha\text{-Bi}_2\text{O}_3$	3×10^{-4}
$\beta\text{-Bi}_2\text{O}_3$	2×10^{-3}
$\gamma\text{-Bi}_2\text{O}_3$	5×10^{-3}
$\delta\text{-Bi}_2\text{O}_3$	1

1.9 Perovskite structured electrolytes

In addition to fluorite structure electrolytes such as stabilized zirconia and ceria, there are many non-fluorite structure oxides which are potentially attractive for SOFC electrolyte application. The crystal structure with ABO_3 stoichiometry is called the perovskite structure where A is a di- or trivalent cation with a large ionic radius and B is a tri- or tetravalent cation with a small ionic radius. Perovskite structured materials are being used as superconductors, refractors, catalysts, magneto resistors and proton conductors [32]. Furthermore, these properties can be modified by changing the processing conditions and selection of proper dopants in A and B sites. Most striking feature of this structure is to contain large concentration of oxide ion vacancies. In other words, the perovskite structures can accommodate cations of wide range of ionic radii and valency. The

perovskite structure will be stable with cubic symmetry when the radii of A- and B- site cations fulfil the requirements of Goldschmidt tolerance factor, $G_t=1$ [33].

1.9.1 Doped perovskite as oxide-ion conductors

Doped $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_3$ (LSGM) was studied independently by Feng et al., [34] and found to exhibit higher ionic conductivity in intermediate temperature range. The highest oxide ion conductivity was found in Sr and Mg doped LaGaO_3 [35, 36] where $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.8}$ system exhibits the maximum conductivity of 0.14 Scm^{-1} at 800°C . Moreover, LaGaO_3 based electrolytes exhibits negligible electronic conductivity and high stability over a wide range of temperatures in comparison with ceria-based electrolyte [37]. In addition to this, they exhibit relatively low thermal expansion similar to that of stabilized zirconia [10]. However, Sr- and Mg- codoped LaGaO_3 system exhibits several drawbacks such as high sintering temperatures required to obtain dense ceramics, segregation of secondary phases during synthesis process and volatilization of gallium oxide during heat treatment at high temperatures [38-41].

1.10 Pyrochlore structured electrolytes

The widespread commercialization of SOFC has caused different challenges due to their high operating temperature. The pyrochlore-type oxides have gained considerable attention because of their good chemical and structural flexibility. Pyrochlore structured materials are considered as oxygen ion-conducting materials since they are considered as $(\text{A}, \text{B})\text{O}_2$ fluorite based structure with one vacant oxygen site per formula unit. These unoccupied sites provide pathways for fast oxygen transport [10]. It is observed that with decrease in A-site cation radius and increase in temperature up to $1377\text{-}2227^\circ\text{C}$, pyrochlores transform into fluorite structure. Pyrochlore structured materials are also being used in various fields of engineering such as sensors, fluorescence and catalytic

activities [42-44]. Compounds with general chemical formula of $A_2B_2O_7$ represent a family of pyrochlores where A is a mono, divalent, trivalent cation and B may be 3d, 4d or 5d transition element. In order to form a stable pyrochlore, A and B cations must have an ionic radius ratio between 1.4 and 1.8 [42]. Structurally, pyrochlore exhibits fluorite type structure AX_2 , except that there are two cation sites and one-eighth of the anions are absent in pyrochlore [45]. In other words, pyrochlore structure can be described as a defective fluorite structure in which cations having variable charge occupy face centered cubic positions whereas seven tetrahedral sites out of 8 available sites are occupied by anions in such a way that charge neutrality of the system is maintained as indicated in figure 1.4. Pyrochlores shows different degrees of disorder in systems of solid solutions by using appropriate substitutions on the A and B sites and when the disorder is complete, then pyrochlores transforms into anion deficient fluorites [46]. In addition to this, geometrical representation of pyrochlore system is indicated in figure 1.5. Moreover, pyrochlore also shows the order and disorder transition due to disordering in cations and /or anions. The magnitude of this disordering depends on the ionic radii difference between cations at the A and B sites. The compounds with similar cationic radii are more likely to form disordered fluorites rather than ordered pyrochlores. Further, the interchangeability of A and B cations enhances the formation of anion Frankel defects which lead to good ionic conductivity in these systems [42, 47]. In other words, the most stable intrinsic defect in defect pyrochlores is an oxygen Frankel pair consisting of a vacant 48f position and interstitial ion occupying an 8b site [46]. The cation disorder increases the similarity between non-equivalent oxygen sites and promotes Frenkel defect formation.

Conclusively, pyrochlore oxides exhibit the following properties:

- ❖ High-temperature stability.
- ❖ Ability to accommodate a wide range of oxygen contents.

- ❖ Change in structural stability due to different cation combinations possible on both A and B sites.
- ❖ Certain pyrochlore compounds are good ion conductors and are potential candidates to be used as electrolytes for SOFCs.

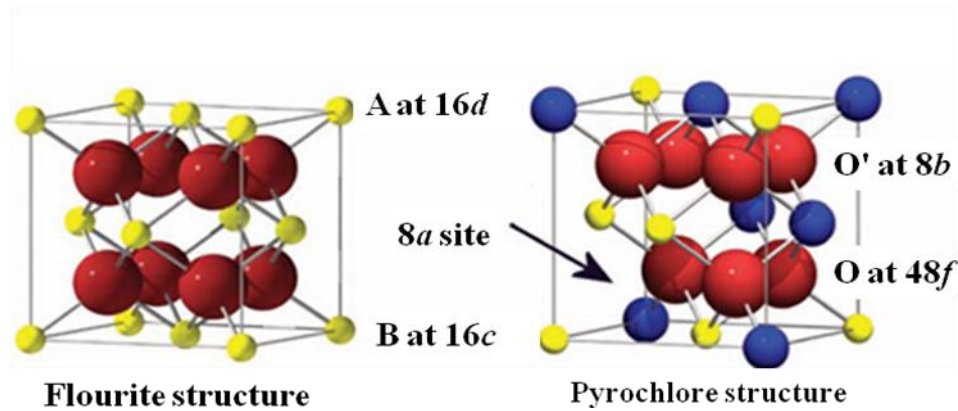


Figure 1.4: Comparison of unit cell of fluorite and pyrochlore structure.

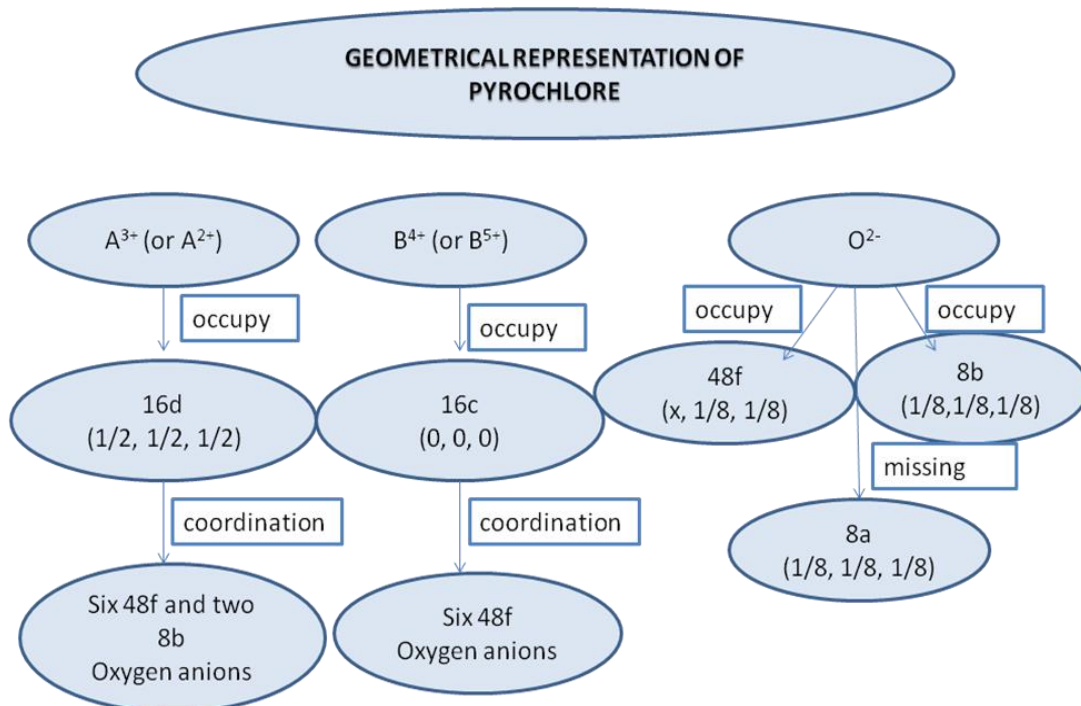


Figure 1.5: Geometrical representation of pyrochlore structure [48].

1.10.1 Doped pyrochlore as oxide-ion conductors

Pyrochlore compounds can be used as solid electrolyte in SOFC [49]. Basically, pyrochlore compounds are inherent ionic conductors whose properties may be altered by changing the processing conditions and doping of different cations on various sites. Acceptor doping of cations in pyrochlores results in enhancement of ionic conductivity e.g, $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{Gd}_2\text{Zr}_2\text{O}_7$ [10]. The highest oxide ion conductivity of 10^{-2} Scm^{-1} was achieved for $\text{Gd}_{2-x}\text{Ca}_x\text{Ti}_2\text{O}_{7-\delta}$ system with $x \sim 0.20$ [49, 50]. Complex oxides with the general formula $\text{Ln}_2\text{Zr}_2\text{O}_7$ (Ln =lanthanide) also exhibits electrical properties which make them potential candidates for SOFC applications [42]. Doped lanthanum zirconate (LZ) pyrochlore (where Rh and Sr were substituted for La in LZ) are used as catalyst for catalytic partial oxidation (CPOX) in fuel cells [51]. Moreover, $\text{Y}_2\text{Zr}_2\text{O}_7$ (YZ) pyrochlores are doped with Bi in order to increase its conductivity and it was found that conductivity value increases with increase in bismuth oxide content at 500°C [7].

1.11 Origin of ionic conduction

Ionic conductivity is because of defect structure which may be point defects (interstitial and substitution) and vacancies which are shown in figure 1.6. Apart from this, Schottky and Frenkel defects also contribute for it as shown in figure 1.7.

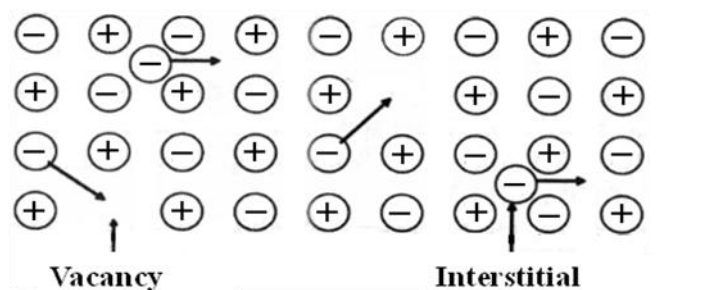


Figure 1.6: The diagram indicating interstitial impurity.

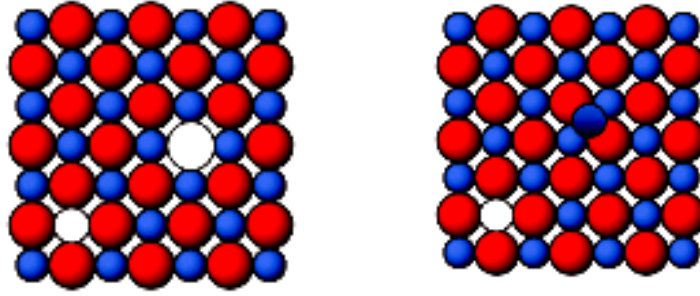
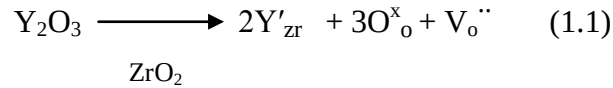
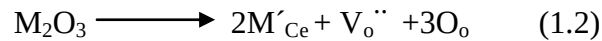


Figure 1.7: (a) Schottky defect and (b) Frenkel defect.

Schottky and Frankel defects are referred as intrinsic defects and associated vacancies are called intrinsic vacancies. The extrinsic vacancies are created in ionic crystals by the addition of impurities in the crystal. For example, the addition of yttria to zirconia introduces oxygen vacancies due to charge compensation effects. For every two Y^{3+} ions taking the place of Zr^{4+} ions, one oxygen vacancy is created to maintain overall charge neutrality. Substitution of Zr^{4+} with Y^{3+} causes the negative net charge in the lattice. The charge neutrality condition is maintained by forming oxygen vacancy written as follows according to Kroger – Vink notation [52].



Where Y'_{Zr} means Y in the Zr site with the apparent negative charge (denoted by the symbol') and V_o'' is the vacancy in the oxygen site with double positive charge (''). O_o^x means the lattice oxygen i.e, oxygen in the oxygen site with net charge of zero (^{x}). Moreover, in case of CeO_2 , oxygen vacancies are created by doping alkaline-earth and rare earth oxides of lower valences:



where M is Sm, Gd or Y as acceptor dopants [10].

1.12 Comparison of electrolyte materials as proton and ionic conductors

Nowadays, proton conducting materials are used as electrolytes in alternative sources of energy for converting chemical to electrical energy. A decrease in operating temperature to $\sim 500^\circ\text{C}$ of SOFC is desirable in order to increase life-time for the fuel cell. Electrolytes based on proton conducting materials have a wide range of applications in fuel cells, batteries, gas sensors etc. Figure 1.8 shows a schematic drawing of SOFC with an electrolyte of proton conducting Ca-doped lanthanum orthoniobate (LaNbO_4) [53]. The fuel i.e., hydrogen, is fed at the anode, is oxidized and electrons are liberated. Protons migrate through the electrolyte as illustrated in figure 1.8. At the cathode side, protons, oxygen and electrons from the external circuit resulting in the formation of water whereas, in case of oxide ion conducting electrolyte, air is reduced to oxygen ions at the cathode side. The oxygen ions migrate through oxygen vacancies in the electrolyte until the fuel (e.g. H_2 , CH_4) is oxidized at the anode and water are produced. However, in both cases electrons are transported through an external circuit from the anode to the cathode and the direct current is utilized in different electrical devices.

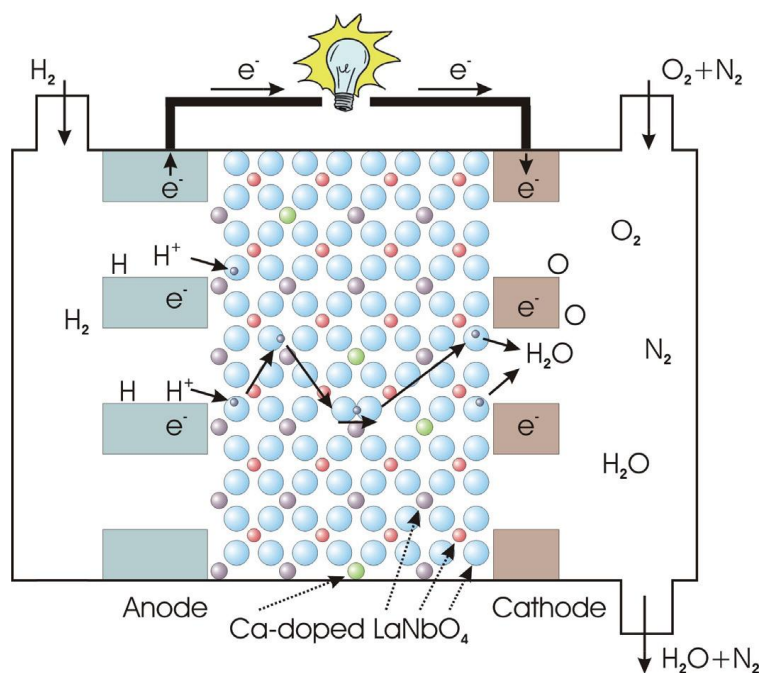
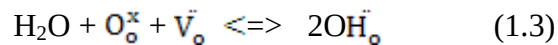


Figure 1.8: Solid oxide fuel cell with proton conducting electrolyte [53].

In comparison to oxide-ion-conducting fuel cells, the proton conducting fuel cells do not require any treatment for purification of fuel due to the fact that in case of proton conducting fuel cells, water is formed at the cathode side. Thus, the advantage using a proton conducting electrolyte results in a fuller utilization of the fuel [53]. In addition to this, the oxide ion conducting SOFCs require high operating temperature to lower ohmic losses whereas, proton-conducting SOFCs can be operated at much lower temperature. Moreover, proton conducting electrolyte materials show higher ionic conductivity, lower activation energy and higher energy efficiency in comparison to oxide ion conductors [54]. The lower activation energy of proton transport results in lowering the operating temperature of SOFC of 450-600 °C. Even though the research on SOFCs has been going on for several decades there are still some challenges to be resolved. A lower operation temperature demanding higher ionic conductivity, new materials with high proton conductivity and stability in CO₂ and H₂O atmosphere are topics that need more attention.

1.12.1 Perovskite as electrolyte materials exhibiting protonic conductivity

Most of the proton conductors are oxides which are doped with transition elements to increase their protonic conductivity. Oxygen-deficient perovskite oxides are oxide ion conductors in dry atmosphere. However, in humid atmosphere they absorb water to fill up oxygen vacancies, incorporate mobile protons into the structure and thus becomes proton conductors. The introduction of protons in the solid oxide network is achieved by doping the B octahedral site with lower valence cations and with the incorporation of hydroxyls in the oxygen-deficient solid in following way [55]:



The proton conductivity of electrolyte is dependent on the concentration of oxygen vacancies in the perovskite oxides [56]. Several perovskite type oxides exhibit high proton conductivity at intermediate temperatures of 450-600 °C and these oxides can be used as electrolyte materials for proton conducting SOFCs.

1.12.2 Pyrochlore as electrolyte materials exhibiting protonic conductivity

The new pyrochlore type compound $\text{K}_{0.88}\text{H}_{1.12}\text{Nb}_2\text{O}_6 \cdot 1.58\text{H}_2\text{O}$ has been investigated for SOFC application [57]. The bulk protonic conductivity comes out to be 10^{-2} Scm^{-1} at 350°C in non-humified air and does not significantly decrease on heating up to 500°C .

1.12.3 Niobates as electrolyte materials exhibiting protonic conductivity

LaNbO_4 is a member of family of rare earth ortho-niobates possessing various properties with multifunctional applications. LaNbO_4 can be used as an electrolyte material candidate in SOFC due to its high proton conductivity at elevated temperatures [58-60]. Lanthanum ortho-niobate (LaNbO_4) exhibits monoclinic-fergusonite crystal system with space group $\text{I}2/a$ at low temperature and tetragonal scheelite system with space group $\text{I}4_1/a$ at high temperature [61]. The phase transformation in LaNbO_4 system is observed in the temperature range of 490°C to 550°C [62, 63]. LaNbO_4 possess ferroelastic behavior at ambient temperature and paraelastic behavior at high temperature and thermal expansion of LaNbO_4 is strongly influenced by ferroelastic to paraelastic phase transition [64, 65]. Moreover, LaNbO_4 based materials are stable in $\text{CO}_2/\text{H}_2\text{O}$ atmosphere and exhibits lower proton conduction of nearly 10^{-3} Scm^{-1} [64-66].

1.13 Other applications of solid oxide electrolytes

The most common commercial application of the solid oxide electrolyte technology is the oxygen sensor. The oxygen sensor is used to control the operation of the exhaust catalyst in an automobile. They are also used in food, metal and burner industries, in which oxygen measurement is required. The currently used YSZ based sensors operates at high temperature over 800°C while desirable operating temperature range (200°C - 400°C) is lower for the sensors. Thus new materials are being developed for its efficient working at lower temperature range [67]. In addition to above, other

applications of solid electrolytes are in solid electrolyte batteries, solid electrolyte thermometer and air separators. In case of solid state battery, the electrolyte is also in solid state and these solid state cells possess many advantages such as miniaturization, long storage life, operation over wide temperature range, rugged structure, no volatilization and no leakage because all the cell components are solids. Moreover, solid electrolytes are used as high temperature electrochemical thermometer. They have the advantage of working at high temperatures greater than 1000°C due to ceramic material used for its construction. However, gas thermometry is limited to a maximum of 1000°C due to lack of suitable material. In addition to this, solid electrolytes have the selectivity to only one type of charge carrier for its use in air separator. The process of air separation is the reverse of oxygen sensors. A device based on this is used to separate oxygen from air particularly from gases, for example, oxygen free nitrogen or argon [68].

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LITERATURE REVIEW

Overview

The purpose of this chapter is to review some of the key developments in the field of oxide as well as protonic conductors pertaining to solid state electrolyte materials of SOFC. The most common solid electrolyte material used in SOFC is yttria-stabilized zirconia and gadolinium doped ceria. Bismuth based fluorite systems have also attracted attention for SOFC application. In terms of other fluorite-related materials, there have been some studies of materials with the pyrochlore structure. Pyrochlore structured materials exhibits a remarkable variety of properties and applications. The conductivity of pyrochlore materials $A_2B_2O_7$ can be increased by two orders of magnitude at 1000 °C by doping on either the A^{3+} or B^{4+} sites. The electrical, thermoelectric, optical, structural properties and thermal conductivity of $Y_2Ti_2O_7$ has been investigated extensively by various researchers. Perovskite materials have also been the subject of great deal of research for SOFC electrolyte applications. In addition to oxide ion conducting materials, proton conducting oxides are also discussed as electrolytes in fuel cells. The main advantage of proton conducting electrolyte is that higher H_2 partial pressure can be achieved as H_2O is produced at the cathode side which results in an improved open-circuit voltage and enhanced efficiency of SOFC systems.

SOFC exhibit several advantages such as high efficiency, high tolerance to impurities in the fuel and flexibility of using various fuels such as hydrogen, carbon dioxide and other categories of hydrocarbon fuels. There are various types of fuel cell components but the main focus of this thesis is on materials which can be used as solid electrolyte for SOFCs. The basic requirement for the solid electrolyte is the high ionic conductivity with low electronic conduction. Moreover, the electrolyte materials must also be chemically and mechanically compatible with other components of fuel cell [1]. In the following section, sequential development of solid electrolytes for its application in electrochemical devices has been reviewed.

Yttria stabilized zirconia possesses pure oxide-ion conductivity as well as excellent chemical and physical stability under reducing and oxidizing atmospheres at an operating temperature of 1000 °C [2-4]. In an attempt to improve the YSZ properties, Liu and Lao [5] recently, added ZnO as a sintering aid to promote densification of the YSZ ceramics. The addition of calcium to YSZ can lead to a reduction in the activation energy for conduction [6]. Moreover, doping with alumina results in increase in mechanical properties and doping with niobium increases defect [6, 7]. Kumar et al. [8] synthesized 20 wt. % nanosize Al_2O_3 doped YSZ composite membrane by tape casting process. The high conductivity of this system was attributed to space charge effect. In addition to this, plaster casting technique is also used to synthesize YSZ. The densities of the samples sintered at 1550°C come out to be 93% [9].

The dielectric relaxation and ac conductivity behavior was studied by Biswas et al., [10] with yttria concentration varying in the range of 10-12 mol%. Luo et al., [11] showed that as gadolinia doped ceria is added to YSZ, a gradual decrease in ionic conductivity has been noticed whereas conductivity of gadolinia doped ceria is higher than that of YSZ. Above observations clearly indicate that undoped YSZ and doped YSZ exhibit good ionic conductivity at 1000°C. However,

to reduce the working temperature of SOFCs (say 700°C) the conductivity of YSZ related systems are not suitable due to sudden drop in conductivity because of structural change.

On the other hand, Gadolinium doped ceria (GDC) has been regarded as promising electrolyte candidate for intermediate temperature SOFCs. Recently, Dong et al., [12] have synthesized $\text{Ce}_{0.79}\text{Gd}_{0.2}\text{Cu}_{0.01}\text{O}_{2-\delta}$ powder and studied the sintering, conductivity, thermal and mechanical properties for its application as intermediate-to-low temperature SOFC. The as synthesized system was found to exhibit electrical conductivity of 0.026 Scm^{-1} at 600 °C and good density was achieved at 1100 °C. The conductivities of CGO i.e., $\text{Ce}_{1-x}\text{Gd}_x\text{O}_2$ ($x=0.1, 0.2$) are higher than those of YSZ or ScSZ at a temperature below 600 °C. The most commonly used dopants for ceria includes samarium, lanthanum, yttrium, ytterbium and neodymium [13-21].

Recently, Xu et al., [22] synthesized $\text{Ce}_{0.85}\text{Sm}_{0.15}\text{O}_{1.925-x}$ at. % $\text{FeO}_{1.5}$ ($x=0, 0.5, 1, 2, 3$) system and found highest conductivity of 0.0597 Scm^{-1} at 800 °C. Another approach to increase the electrical conductivity of ceria is by co-doping. Ceria co-doped with Y_2O_3 (10 mol%)- Sm_2O_3 (10 mol%) and Nd_2O_3 (9 mol%)- Sm_2O_3 (9 mol%) shows increase in ionic and grain conductivity respectively, at low temperature [23, 24]. Liu et al., [25] have investigated that ceria co-doped with Sm^{3+} and Nd^{3+} has an electrical conductivity of $1.0 \times 10^{-2} \text{ Scm}^{-1}$ at 481 °C.

SOFCs using ceria-carbonate composite electrolytes and Ni-based electrodes have resulted in improved cell performances below 600 °C [26, 27]. Recently, Fan et al., [28] have studied samaria doped ceria-carbonate (SCC) composite exhibiting good chemical compatibility and thermal matching with Ni-based electrodes.

$\text{Ce}_{0.8}\text{Pr}_{0.2}\text{O}_2$ (CPO) nanoparticles were first time synthesized by Larramendi et al., [29] with the help of polyol modified method and high purity nanoparticulate powder was obtained with a size range between 2 and 3 nm. The better performance of CPO nanoparticles was mainly attributed to their higher specific area and lower bulk size which helps in better oxygen ion diffusion through the material.

Bismuth based fluorite systems have also attracted considerable attention as electrolyte material for SOFC. Praseodymium (Pr) and Zirconia (ZrO_2) doped Bi_2O_3 were synthesized and studied by Naumovich et al., [30]. Doping of bismuth oxide is done to stabilize the conductive phase at low oxygen partial pressure and temperature. One such phase of doped bismuth oxide is $\text{Bi}_3\text{Nb}_{0.1}\text{Zr}_{0.9}\text{O}_{6.55}$ which remains stable at lower temperature [31]. The conductivity versus $1/T$ plots for some electrolyte materials are given in figure 2.1.

Some studies suggest that doping of Bi_2O_3 with rare earth elements is not able to stabilize the fcc phase completely. So, double stabilizers are used which increases the stability of the material with time for example, codoping with other metals such as Nb and W [32-36]. $(\text{Bi}_2\text{O}_3)_{0.735}(\text{Er}_2\text{O}_3)_{0.21}(\text{WO}_3)_{0.055}$ shows a conductivity of 0.05 Scm^{-1} at 550°C and $(\text{BiO}_{1.5})_{0.88}(\text{DyO}_{1.5})_{0.08}(\text{WO}_3)_{0.04}$ has a conductivity of 0.043 Scm^{-1} at 500°C [37].

In addition to this, $\text{Bi}_4\text{V}_2\text{O}_{11}$ systems have been studied in order to achieve higher ionic conductivity by doping at V and Bi site by Kant et al., [38]. The systems of $\text{Bi}_4\text{V}_{2-x}\text{Cu}_x\text{O}_{11-\delta}$, $\text{Bi}_4\text{V}_{2-x}\text{Mn}_x\text{O}_{11-\delta}$, $\text{Bi}_4\text{V}_{2-x}\text{Ti}_x\text{O}_{11-\delta}$ and $\text{Bi}_4\text{V}_{2-x}\text{Al}_x\text{O}_{11-\delta}$ were found to stabilize with γ – phase for $x \geq 0.2$. The conductivity of pure $\text{Bi}_4\text{V}_2\text{O}_{11}$ was observed to be 1.12×10^{-6} at 300°C . The highest conducting $\text{Bi}_4\text{V}_{2-x}\text{Ti}_x\text{O}_{11-\delta}$ system follows the conductivity order as $\sigma_{0.4} > \sigma_{0.3} > \sigma_{0.2} > \sigma_{0.1}$ in terms of composition and $\sigma_{800^\circ\text{C}} > \sigma_{825^\circ\text{C}} > \sigma_{775^\circ\text{C}} > \sigma_{750^\circ\text{C}}$ in terms of sintering temperature.

Another category of materials that has been investigated for potential electrolyte materials are the pyrochlore. In the solid oxide fuel cell area, pyrochlore oxides have received attention because of their high-temperature stability and ability to accommodate a wide range of oxygen contents and cations on both A and B sites. The similarity of this structure with the cubic fluorite structure indicates that it may be a good oxygen ion conductor since it possesses structure in which one oxygen per unit cell is missing. This unoccupied site provides pathways for fast oxygen transport. It was observed that at elevated temperature (1377-2227 °C), most of the pyrochlores change into fluorite structure. Research is going on all over the world to search for the electrolytes materials which possess pyrochlore structure [39, 40]. The structural ordering/disordering in pyrochlores is strongly correlated with the average A to B cation size ratio. The stability of zirconates and titanates possessing pyrochlore structure are found to be in the range of 1.46 to 1.80 [41]. The conductivity of $A_2B_2O_7$ pyrochlore materials can be increased by two orders of magnitude at 1000 °C by doping on either the A^{3+} or B^{4+} sites. The A^{3+} sites in the pyrochlore $A_2Ti_2O_7$ ($A=Y, Sm, Gd$) can be doped with M^{2+} cations such as Ca^{2+} and Ti^{4+} sites with Al^{3+} . The above doping results in generation of oxygen vacancies due to difference between the oxidation state of the dopants and A, B site cations (Ca^{2+} and Al^{3+} ions) [42, 43].

The highly conductive materials with the pyrochlore structure are titanates. Since there are absence of d-electrons (Ti^{4+} : d^0 system) and the f-electrons are localized in the inner 4f levels, so electronic conductivity is not observed at room temperature e.g., $Ln_2Ti_2O_7$ is found to be insulating with $10^{-12} \text{ Scm}^{-1}$ at room temperature. Whereas, p-type conduction has been observed by Brixner et al., [44] at temperature of 1000 °C.

Uematsu et al., [45] have predicted that oxide-ion conduction may be observed in some titanates with increasing temperature. Tuller et al., [46] have reported oxide-ion conductivity of $\text{Gd}_2\text{Ti}_2\text{O}_7$ pyrochlore as $6.3 \times 10^{-4} \text{ Scm}^{-1}$ at 1000°C in air. Mori et al., [47] have studied the crystal structure, electrical conductivity and thermal expansion of $\text{Gd}_x\text{Ti}_2\text{O}_{7-\delta}$ pyrochlores ($1.72 \leq x \leq 2.10$). It was observed that A-site deficiency of $\text{Gd}_x\text{Ti}_2\text{O}_{7-\delta}$ promotes the sintering characteristics of the material. However, the electrical conductivity of pyrochlores with A-site vacancies was found to be lower than $\text{Gd}_x\text{Ti}_2\text{O}_7$ in air.

This conductivity is further enhanced by acceptor-type doping on the cationic sites. The highest level of oxygen ionic conduction in pyrochlore-type structures is achieved for $\text{Gd}_{2-x}\text{Ca}_x\text{Ti}_2\text{O}_{7-\delta}$ with $x=0.20$ [48, 49]. The incorporation of calcium into the lattice of $\text{Gd}_2\text{Ti}_2\text{O}_{7-\delta}$ increases the p-type electronic conduction and decreases the n-type contribution to the total conductivity. The values of oxygen ion transference numbers of $\text{Gd}_{1.9}\text{Ca}_{0.1}\text{Ti}_2\text{O}_{7-\delta}$ in pure oxygen was found to be high i.e., 0.90-0.95 at $800\text{-}950^\circ\text{C}$ [43].

Kharton et al., [50] investigated the oxygen ion transference numbers of $\text{Gd}_{2-x}\text{Ca}_x\text{Ti}_2\text{O}_{7-\delta}$ ($x=0.10\text{-}0.14$) pyrochlore system at $700\text{-}950^\circ\text{C}$ by the modified electro motive force and Faradaic efficiency techniques. The ion transference numbers came out to be between 0.95-0.98 in air. The thermal expansion coefficient of the system comes out to be $(10.4\text{-}10.6) \times 10^{-6} \text{ K}^{-1}$ at $127\text{-}1027^\circ\text{C}$ in air.

Kramer et al., [42] have chosen acceptor dopants i.e., Ca and Al which were incorporated substitutionally into the “A” site and “B” site respectively in $(\text{Gd}_{1-x}\text{A}_x)_2(\text{Ti}_{1-y}\text{B}_y)_2\text{O}_7$ lattice. The activation energy was found to decrease from 0.94 eV to 0.63 eV for the “A” site Ca doped samples with x lying between 0.0 and 0.1. In addition to this, increase in ionic conductivity and decrease in activation energy was observed for “B” site Al doping up to a doping level of $y=0.01$

in $\text{Gd}_2(\text{Ti}_{1-y}\text{Al}_y)_2\text{Ti}_2\text{O}_7$ system. The solid solubility limit of Al doping in $\text{Gd}_2(\text{Ti}_{1-y}\text{Al}_y)_2\text{Ti}_2\text{O}_7$ system was found to be $y \leq 0.01$.

Another doped system $(\text{Ln}_{0.9}\text{Ca}_{0.1})_2\text{Ti}_2\text{O}_7$ ($\text{Ln} = \text{Gd}, \text{Y}$ and Yb) has been found to exhibit high oxide ion conductivity at high temperatures and $\text{Gd}_2(\text{Ti}_{1-x}\text{Mo}_x)_2\text{O}_7$ ($0.1 \leq x \leq 0.7$) shows high electronic conductivity under reducing atmospheres which make such materials potentially useful as electrolyte as well as anode materials in SOFCs [42, 43, 51, 52].

In addition to this, yttrium titanate, $\text{Y}_2\text{Ti}_2\text{O}_7$, is an important member of the pyrochlore family because it exhibits various properties which make it suitable for potential applications in different fields. $\text{Y}_2\text{Ti}_2\text{O}_7$ is a material having pyrochlore structure with Y^{3+} occupying A-site and Ti^{4+} occupying B-site. The electrical, thermoelectric, optical, structural properties and thermal conductivity of $\text{Y}_2\text{Ti}_2\text{O}_7$ have been investigated extensively by various researchers [53-55].

Uematsu and co-workers [45] have reported that yttrium titanate ($\text{Y}_2\text{Ti}_2\text{O}_7$) exhibits n-type conductivity at lower partial pressure of oxygen (p_{O_2}) while oxide ion conductivity was observed at high oxygen pressure. Doping of different cations in $\text{Y}_2\text{Ti}_2\text{O}_7$ system plays an important role. It was observed that conductivity of $(\text{Y}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7$ for $x=0.1$ system increases by two orders of magnitude in comparison with pure compound at 1000°C . In addition to this, $(\text{Y}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7$ system with $x=0.0, 0.01, 0.02, 0.05$ and 0.10 , ionic conduction increases with decrease in temperature and increase in Ca concentration [56]. In $\text{Y}_2(\text{Ti,Zr})_2\text{O}_7$ system, introduction of 50% Zr initiates disorder between cationic sites and 90% Zr results in the complete disorder among the cationic sites and oxygen sites resulting in the formation of defect-fluorite structure at room temperature [57]. However, in $\text{Y}_2(\text{Zr}_y\text{Ti}_{1-y})_2\text{O}_7$ ($0 \leq y \leq 0.9$) system, transition from single-phase pyrochlore to single-phase “defect fluorite” around $y=0.6$ composition is observed [58, 59]. In $\text{Y}_2(\text{Sn}_y\text{Ti}_{1-y})_2\text{O}_7$ ($0 \leq y \leq 1$) system high degree of ordering was observed. However, mixed occupancy

of B-site by Sn^{4+} and Ti^{4+} was reported [59]. Another chemical composition of $\text{A}_2\text{Ti}_2\text{O}_7$ ($\text{A} = \text{Sm}, \text{Gd}, \text{Y}$) with Ca^{2+} , Sr^{2+} substituting “A” site and Al^{3+} , Ru^{4+} substituting “B” (Ti) site whereas Mg^{2+} substituting both “A” or “B” site was reported [50].

Moreover, $\text{Y}_2\text{Zr}_2\text{O}_7$ (YZ) pyrochlores are doped with Bi in order to increase its conductivity and it was found that conductivity value increases with increase in bismuth oxide content at 500 °C [60].

Mandal et al., [61] have also studied rare earth zirconates exhibiting pyrochlore structure. $\text{Gd}_2\text{Zr}_2\text{O}_7$ system was chosen where doping at the Gd site with isovalent rare-earth cations like Nd was done. The electrical conductivity was found to increase at 349-423 °C. In addition to this, gadolinium zirconate is known to exist in two crystal forms, i.e, highly disordered pyrochlore (P- $\text{Gd}_2\text{Zr}_2\text{O}_7$) and anion deficient fluorite (F- $\text{Gd}_2\text{Zr}_2\text{O}_7$) [62]. The P- $\text{Gd}_2\text{Zr}_2\text{O}_7$ ionic conductivity can be improved by aliovalent substitutions at A and B cation sites (e.g., Ca^{2+} or Sr^{2+} for Gd^{3+} ; Al^{3+} or Sc^{3+} for Zr^{4+}) [63, 64]. Moreover, it was found that La substitution for Gd in $\text{Gd}_2\text{Zr}_2\text{O}_7$ system does not affect its ionic conductivity for $y \leq 0.8$ [65]. Moreover, the electrical properties of $\text{Gd}_2(\text{B}_{1-y}\text{Zr}_y)_2\text{O}_7$ ($\text{B} = \text{Ti}^{4+}$ or Sn^{4+}) have been studied and it was found that with increase in Ti content the bulk dc conductivity remains almost constant for $y \geq 0.4$ [66-70]. Liu et al., [71] have studied the electrical conductivity of $(\text{Sm}_{1-x}\text{Yb}_x)_2\text{Zr}_2\text{O}_7$ ($0 \leq x \leq 1.0$) over a frequency range of 200 Hz to 20MHz from 450 to 900°C in air. The grain conductivity of $(\text{Sm}_{1-x}\text{Yb}_x)_2\text{Zr}_2\text{O}_7$ system increases with increasing temperature and attains the highest value of $1.71 \times 10^{-2} \text{ Scm}^{-1}$ at 900°C. Moreover, $(\text{Sm}_{1-x}\text{Gd}_x)_2\text{Zr}_2\text{O}_7$ ($0 \leq x \leq 1.0$) ceramics were synthesized by pressure less-sintering method and the electrical conductivity was found to be maximum for $\text{SmGdZr}_2\text{O}_7$ in the temperature range of 350-600°C [72].

Wuensch et al., [59] have investigated the ionic conductivity and degree of disorder of various pyrochlore systems $Y_2(Zr_yTi_{1-y})_2O_7$, $Y_2(Sn_yTi_{1-y})_2O_7$, $Y_2(Zr_ySn_{1-y})_2O_7$ and $Gd_2(Sn_yTi_{1-y})_2O_7$ ($y=0$ to 1). Sn-Ti solid solutions were found to retain on ordered pyrochlore structure for all values of y and yttrium pyrochlores were found to be more disordered than the gadolinium system. $Y_2(Zr_ySn_{1-y})_2O_7$ samples were found to exhibit significant amount of disordered fluorite-like phase whose diffraction maxima closely coincides with the peaks of the pyrochlore phase. $Y_2(Zr_{0.6}Ti_{0.4})_2O_7$ system was found to have highly-disordered cation arrangements which remain unchanged up to 1250°C and oxygen-ion conductivity was found to be greater than 10^{-2} Scm^{-1} at 1000°C.

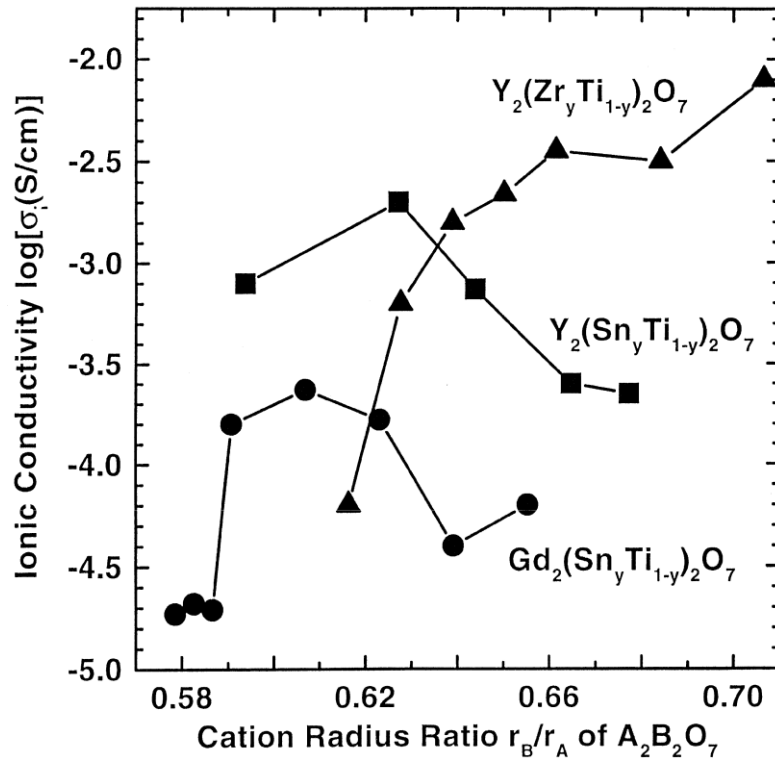


Figure 2.1: The ionic conductivity at 1000 °C as a function of the radius ratio R_B/R_A or the solid solutions $Y_2(Zr_yTi_{1-y})_2O_7$, $Y_2(Sn_yTi_{1-y})_2O_7$ and $Gd_2(Sn_yTi_{1-y})_2O_7$ [59].

The perovskite $LaGaO_3$ doped with strontium and magnesium $La_{1-x}Sr_xGa_{1-y}Mg_yO_3$ (LSGM) are used as electrolyte materials because of their good oxygen-ion conductivity [73]. Recently,

freeze-drying method is used for the synthesis of dense LSGM ceramics. The conductivity of LSGM can be increased by doping with transition metals such as cobalt and iron [13, 74-78]. Both the dopants increase the conductivity especially at low temperature. Recently, $\text{La}_{0.7}\text{Sr}_{0.3}\text{Ga}_{0.7}\text{Mg}_{0.1}\text{Fe}_{0.2}\text{O}_{3-\delta}$ system has been reported as a new attractive substitute for solid electrolytes which are produced by solid state reaction method based on calcination [79]. Moreover, lanthanum based perovskites including LaScO_3 , LaInO_3 , LaYO_3 and LaAlO_3 based materials are also used as oxygen ion conductors and find application as electrolyte material for SOFC [60, 80]. Recently, Sinha et al., [81] prepared undoped and Ca-doped GdAlO_3 systems. These systems exhibited good sinter ability leading to high experimental density. Kakinuma et al., [82] have studied the behavior of SOFC in which $(\text{Ba}_{0.3}\text{Sr}_{0.2}\text{La}_{0.5})\text{InO}_{2.75}$ was used as an electrolyte material and found power density to be maximum at 800 °C.

In addition to oxide ion conducting materials, proton conducting oxides have been investigated as electrolytes in fuel cells [83]. The main advantage of proton conducting electrolyte (SOFC- H^+) is that higher H_2 partial pressure can be achieved as H_2O is produced at the cathode side which results in an improved open-circuit voltage and enhanced efficiency of SOFC systems [84]. Moreover, proton conducting SOFCs helps in decreasing the working temperature and ultimately reduces the cost.

Significant proton conductivity has been reported for some pyrochlore systems such as $\text{La}_2\text{Zr}_2\text{O}_7$ -based systems, where proton incorporation is promoted by doping with lower valent cations on the A- or B- sites [85]. Higher proton conductivities were found on the A-site doping i.e., $(\text{La}_{1.95}\text{Ca}_{0.05})\text{Zr}_2\text{O}_{7-\delta}$ system exhibiting conductivity of $6.8 \times 10^{-4} \text{ Scm}^{-1}$ at 600 °C which was

three times higher than the system doped on the B-site [86-89]. Moreover, acceptor doped pyrochlore materials such as $\text{Er}_{1.96}\text{Ca}_{0.04}\text{Ti}_2\text{O}_{7-\delta}$ was found to exhibit high level of proton mobility in the grain boundaries whereas, the bulk conductivity showed no dependence on the presence of water vapor [90]. In addition to this, proton conductivity was studied in another system such as $\text{Sm}_{1.92}\text{Ca}_{0.08}\text{Ti}_2\text{O}_{7-\delta}$ and $\text{Sm}_2\text{Ti}_{1.92}\text{Y}_{0.08}\text{O}_{7-\delta}$ [89]. An increase in bulk conductivity was observed for both the samples below 500 °C for wet conditions. The A-site doped sample, $\text{Sm}_{1.92}\text{Ca}_{0.08}\text{Ti}_2\text{O}_{7-\delta}$ displayed higher proton conductivity compared with B-site doped phase. Recently, the electrochemical impedance spectroscopy (EIS) was carried out on $\text{Sm}_{1.92}\text{Ca}_{0.08}\text{Ti}_2\text{O}_{7-\delta}$ system to determine the conductivity as a function of p_{O_2} in dry and wet atmospheres and at various temperatures [91]. Further EMF were carried out to determine the transport numbers associated with the conduction processes. The combined EIS and EMF measurements showed that the conduction in $\text{Sm}_{1.92}\text{Ca}_{0.08}\text{Ti}_2\text{O}_{7-\delta}$ system is mainly ionic. The oxide ion transport dominates with a transport number $t_{\text{O}} > 0.98$ and proton conduction dominates at 300 and 400°C in wet conditions.

On the other hand, the disordered fluorite structure could also be used as the electrolyte for the intermediate temperature SOFCs. Tao et al., [92] have investigated the chemical stability of the $\text{La}_{1.95}\text{Ca}_{0.05}\text{Ce}_2\text{O}_{7-\delta}$ (LCCO) powders under atmosphere of 3% CO_2 and 3% H_2O at 700 °C for 100 h. A fuel cell with LCCO electrolyte was prepared using the suspension spray method and was tested in the temperature range from 600°C to 700°C. The maximum power density of the single cell was found to be 259 Wcm^{-2} at 700°C.

Patcharavorachot et al., [93] investigated a combined SOFC system with different electrolytes (SOFC-O^{2-} and SOFC-H^+). The exhaust gas from SOFC-O^{2-} is directly fed into SOFC-H^+ . The

performance of the SOFC-O²⁻-SOFC-H⁺ system provides a higher efficiency (54.11%) in comparison with the use of single SOFC.

The most common proton-conducting oxide is BaCeO₃ which has been doped with various oxides such as samarium [94], neodymium [95, 96] and ytterbium [97] so that they can be used in SOFC. In addition to this, other proton conducting oxides for use in SOFC include BaSc_{0.5}Zr_{0.5}O₃, (La,Pr)_{0.9}Ba_{1.1}GaO_{3.95} and Nd_{0.8}Ba_{1.1}GaO_{3.95} [98, 99].

Zirconate-based ceramics SrZr_{1-x}Y_xO_{3-δ} have the high chemical stability as well as high proton conductivity and are expected to be applied to fuel cells [100]. Moreover, Iwahara et al., [101-105] found that SrCeO₃ and BaCeO₃ materials exhibit protonic conductivity in an atmosphere containing hydrogen at high temperature. It was found that when Y³⁺, Sc³⁺, Yb³⁺ were partially substituted for cerium then protonic conduction increases in an atmosphere of hydrogen or water vapor at high temperature. Doped BaCeO₃ and BaZrO₃ exhibits high proton conductivity in hydrogen and/or water vapour atmospheres [106-108]. However, Y-doped BaZrO₃ needs high sintering temperatures that lead to high cost and difficulty in choosing a compatible electrode material for electrode-supported fuel cells [109]. On the other hand, poor sinteractivity leads to large grain boundary volume content which results in decrease in protonic conductivity. Thus, the BaZrO₃ sinteractivity needs to be improved for its practical applications. The methods used to improve the sinteractivity of BaZrO₃ are the use of sintering aids (such as ZnO and NiO) and introduction of a second dopant (such as Pr) [110-112]. Ito et al., [113] have found that introduction of In³⁺ as the second dopant to Y-doped BaZrO₃ can lead to slightly better sinteractivity. Recently, In³⁺ was successfully used as the single dopant for BaZrO₃ to improve the sinteractivity [114]. The doped BaZrO₃ (BaZr_{0.7}In_{0.3}O_{3-δ}) system showed an improved grain boundary proton conductivity of 1.7 x 10⁻³ Scm⁻¹ at 700 °C in wet 10% H₂ atmosphere.

In addition to perovskite materials, other structural materials such as LaNbO_4 have also been used as the electrolyte for proton-conducting SOFCs due to its high stability [115]. Moreover, $\text{La}_{1.95}\text{Ca}_{0.05}\text{Ce}_2\text{O}_{7-\delta}$ system possessing fluorite structure has also been investigated as electrolyte material for SOFC [92].

Doping of La^{3+} site by Ca^{2+} results in the improvement of ionic conductivity due to the formation of oxygen vacancies [116]. Moreover, $\text{La}_{0.995}\text{Ca}_{0.005}\text{NbO}_{4-\delta}$ (LCN) compound has been doped by partial substitution of La by Ce, Pr and Nb by Mn, W, Cr respectively in order to improve the electronic conductivity of LCN [117]. Lin et al., [118] fabricated stable proton conducting $\text{La}_{0.99}\text{Ca}_{0.01}\text{NbO}_4$ thin electrolyte membrane for protonic ceramic membrane fuel cells (PCMFCs). Tolchard et al., [119] investigated chemical compatibility of proton conducting electrolyte material LaNbO_4 with LaMO_3 (M= Mn, Fe, Co) perovskite materials. LaNbO_4 was found to exhibit good chemical stability with LaMO_3 perovskites since LaFeO_3 and LaMnO_3 systems show no reaction with LaNbO_4 . Fjeld et al., [120] measured grain boundary as well as grain interior conductivities of 0.5% Sr doped LaNbO_4 at 400°C and found that specific grain boundary conductivity is 4 orders of magnitude lower than the interior grain conductivity. The conductivity of acceptor doped LaNbO_4 have been investigated in the temperature range of 300°C to 1200°C as a function of oxygen and water vapor pressure [121]. 1% acceptor doping of LaNbO_4 results in proton conductivity of 0.001Scm^{-1} at 950°C . In addition to this, acceptor doping with Ca or Sr results in highest proton conductivity of the orthoniobate/ orthotantalate series $\sim 1 \times 10^{-3} \text{Scm}^{-1}$ in wet reducing conditions at 800°C [122].

It is found that oxygen vacancy concentration in the ABO_4 materials remains approximately 10 times lower than that of common perovskite proton conductors due to very low solubility of A-site acceptor dopants in the fergusonite structure [121, 123-125]. This leads to low number of

protonic charge carriers and low levels of conductivity. In order to increase the electrical conductivity acceptor doping on the B-site of ABO_4 was done which results in formation of more oxygen vacancies. The introduction of smaller isovalent cation on the B-site of ABO_4 compositions was found to stabilize the scheelite phase to room temperature which results in good proton conductivity at lower temperature [126]. Further, B-site dopants in $\text{LaNb}_{1-x}\text{M}_x\text{O}_{4-\delta}$ materials with $\text{M} = \text{Ga, Ge, Si, Al, B, P, Zr or Ti}$ were chosen to investigate them as good proton conductors [127]. The solubility limit of these cations was found to be very low ($x \leq 0.03$). The electrical properties of Ti-doped compositions were studied. Higher bulk and total conductivities were observed in wet than dry atmosphere indicating significantly high protonic contribution to total conductivity. However, the activation energy of $\text{LaNb}_{0.98}\text{Ti}_{0.02}\text{O}_{4-\delta}$ was found too much higher than that of A-site Sr-doped material ($\text{Sr}_{0.02}\text{La}_{0.98}\text{NbO}_{4-\delta}$). The Sr-doped composition exhibits higher conductivities than the Ti-doped compositions up to 900°C .

Lein et al., [128] have synthesized asymmetric membranes of proton conducting $\text{La}_{0.995}\text{Sr}_{0.005}\text{NbO}_4$ system by aqueous tape casting of porous substrates and depositing them by spray coating. The high temperature proton conducting fuel cell has been made with $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ as the cathode, $\text{La}_{0.995}\text{Sr}_{0.005}\text{NbO}_4$ as the electrolyte and $\text{Ni-La}_{0.995}\text{Sr}_{0.005}\text{NbO}_4$ cermet as the anode.

Currently, LaNbO_4 -based proton conducting fuel cells are being manufactured. Magraso and Fontaine [129] investigated the compatibility between NiO and niobate phases by depositing a thin layer of electrolyte by wet ceramic coating on NiO-LaNbO_4 based anode and co-sintered at $1200\text{--}1300^\circ\text{C}$. It was found that NiO does not react with Ca-doped LaNbO_4 whereas, fast reaction of NiO was found to occur with La_3NbO_7 and LaNb_3O_9 phases. La_3NbO_7 and NiO form

a mixed conducting perovskite $\text{LaNi}_{2/3}\text{Nb}_{1/3}\text{O}_3$ phase, while LaNb_3O_9 and NiO forms either NiNb_2O_6 or $\text{Ni}_4\text{Nb}_2\text{O}_9$ phase depending on the annealing temperature.

Recently, Waldbillig and Kesler [130] investigated the electrochemical performance of plasma sprayed SOFCs with three different electrolytes having different microstructures and thicknesses. Further, the effects of electrolyte microstructure and thickness were studied on electrochemical properties such as open circuit voltage (OCV) and series resistance (R_s). The OCV values comes out to be approximately 90% of the Nernst voltages and electrolyte area specific resistance of $0.1 \Omega\text{cm}^2$ were obtained at 750°C for electrolyte thicknesses below $20 \mu\text{m}$. It was found that highly dense electrolyte layers were produced from high plasma gas flow rate conditions, highest OCV values with lowest total electrolyte-related losses. On the other hand, medium flow rate conditions result in more permeable electrolyte layers that has lower OCV values and higher total electrolyte-related losses whereas, low flow rate coatings were found to exhibit poor electrolyte microstructures with high permeability, low OCV values and high R_s values.

After analyzing the entire literature work, it seems that pyrochlore structured materials ($\text{A}_2\text{B}_2\text{O}_7$) exhibit a good ionic conductivity over a vast range of composition and oxygen vacancies can be created by acceptor doping on A and B sites. Among the various studied pyrochlore materials, titanate pyrochlores e.g., $\text{Gd}_2\text{Ti}_2\text{O}_7$ had been reported as the most promising one due to their stability from low temperature region to high temperature region with good ionic conductivity in the temperature region of 1000°C . However, doping of SrO on $\text{Y}_2\text{Ti}_2\text{O}_7$ is less studied system. In the present work, it has been planned to investigate the effect of systematic doping of SrO , CaO for Y_2O_3 as well as La_2O_3 in $\text{Y}_2\text{Ti}_2\text{O}_7$ and $\text{La}_2\text{Ti}_2\text{O}_7$ system. Different concentration of Sr^{2+} and Ca^{2+} doping was chosen to find the solid solubility limit and its affect on conductivity. The results are discussed in light of oxygen vacancies, order and disorder transitions using electrical

conductivity, X-ray analysis, Fourier Transform-Infrared Spectroscopy, thermal expansion coefficient (TEC) and scanning electron microscope (SEM) in-order to check their suitability for SOFC. Moreover, fergusonite structured materials (ABO_4) are also used as electrolytes in SOFC due to their high proton conductivity at elevated temperatures. Recently, acceptor doped (Ca, Sr)LaNbO₄ system which is stable in operating atmospheres have been reported as candidates for proton conducting electrolytes and these materials were hence, chosen for the present studies. The effect of acceptor doping (Sr, Ca) on A-site of ABO_4 (A=La, Y) materials were further investigated. But there are still challenges to overcome for pyrochlore as well as fergusonite based materials before the materials can be fully utilized as oxide ion conductors in SOFCs. Moreover, a correlation among various parameters is still required to check their suitability and applicability as an electrolyte for SOFC.

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EXPERIMENTAL PROCEDURES

Overview

In this chapter, the various steps employed for the synthesis of different systems from initial ingredients are described in detail. The solid state reaction method required for synthesis of different composition is discussed. Various techniques which are used to characterize the samples are given. We have developed $\text{SiO}_2\text{-BaO-ZnO-}x\text{B}_2\text{O}_3\text{-(10-x)Y}_2\text{O}_3$ glasses as sealing material for SOFC which are found to exhibit good thermal stability without the formation of any detrimental phase during the prolonged heat treatment. At the same time one of our doped pyrochlore systems $\text{Y}_2\text{Ti}_2\text{O}_7$ has also exhibited good conductivity and thermal stability. Considering these aspects the interaction study of these two systems $\text{Y}_2\text{Ti}_2\text{O}_7$ (electrolyte) and $40\text{SiO}_2.30\text{BaO}.20\text{ZnO}.10\text{Y}_2\text{O}_3$ based glasses have been done for the study of chemical interactions between them to understand the kinetics of the formation of different crystalline phases with respect to the heat treatment temperature and duration. The details of the instruments, their working procedures and operating conditions are also described in detail. As prepared samples after sintering were characterized by X-ray diffraction (XRD), thermal gravimetric analysis (TGA) /differential thermal analysis (DTA), fourier transform infra-red spectroscopy (FT-IR), dilatometer and scanning electron microscopy (SEM). The gold sputtered pellets were used to measure a.c. conductivity.

3.1 Initial raw materials

In the present study, initial ingredients used for the synthesis of the samples were Y_2O_3 (99.9%, Sigma Aldrich), TiO_2 (99.9%, Sigma Aldrich), Ti_2O_3 (99.9%, Sigma Aldrich), SrO (99.9%, Sigma Aldrich), Nb_2O_5 (99.9%, Sigma Aldrich), La_2O_3 (99.9%, CDH) and CaO (99.9%, CDH). All these materials were used without any further purification.

3.2 Sample preparation

Sample system along with their compositions and label are given in the table 3.1(a, b) respectively. For sample preparation, the following procedure was adopted:

Table 3.1 (a): Sample systems with their names.

Sample Systems	Sample Name	Composition
$\text{Y}_{1-x}\text{M}_x\text{TiO}_y$ (M= Sr, Ca)	YST	$\text{Y}_2\text{O}_3+\text{TiO}_2$ (x=0)
$\text{La}_{1-x}\text{M}_x\text{TiO}_y$ (M= Sr, Ca)	LST	$\text{La}_2\text{O}_3+\text{TiO}_2$ (x=0)
$\text{Y}_{1-x}\text{M}_x\text{NbO}_y$ (M= Sr, Ca)	YNS	$\text{Y}_2\text{O}_3+\text{Nb}_2\text{O}_5$ (x=0)
$\text{La}_{1-x}\text{M}_x\text{NbO}_y$ (M= Sr, Ca)	LNS	$\text{La}_2\text{O}_3+\text{Nb}_2\text{O}_5$ (x=0)

Table 3.1 (b): Sample compositions with their names.

Sample System	Sample Name	Composition	Sample Name	Composition
$Y_{1-x}M_xTiO_y$ (M= Sr, Ca)	YST-1	$Y_2O_3+TiO_2+SrO$ (x=0.1)	YCT-1	$Y_2O_3+TiO_2+CaO$ (x=0.1)
	YST-2	$Y_2O_3+TiO_2+SrO$ (x=0.2)	YCT-2	$Y_2O_3+TiO_2+CaO$ (x=0.2)
	YST-3	$Y_2O_3+TiO_2+SrO$ (x=0.3)	YCT-3	$Y_2O_3+TiO_2+CaO$ (x=0.3)
	YST-4	$Y_2O_3+TiO_2+SrO$ (x=0.4)	YCT-4	$Y_2O_3+TiO_2+CaO$ (x=0.4)
$La_{1-x}M_xTiO_y$ (M= Sr, Ca)	LST-1	$La_2O_3+TiO_2+SrO$ (x=0.1)	LCT-1	$La_2O_3+TiO_2+CaO$ (x=0.1)
	LST-2	$La_2O_3+TiO_2+SrO$ (x=0.2)	LCT-2	$La_2O_3+TiO_2+CaO$ (x=0.2)
	LST-3	$La_2O_3+TiO_2+SrO$ (x=0.3)	LCT-3	$La_2O_3+TiO_2+CaO$ (x=0.3)
	LST-4	$La_2O_3+TiO_2+SrO$ (x=0.4)	LCT-4	$La_2O_3+TiO_2+CaO$ (x=0.4)
$Y_{1-x}M_xNbO_y$ (M= Sr, Ca)	YNS-1	$Y_2O_3+Nb_2O_5+SrO$ (x=0.1)	YNC-1	$Y_2O_3+Nb_2O_5+CaO$ (x=0.1)
	YNS-2	$Y_2O_3+Nb_2O_5+SrO$ (x=0.2)	YNC-2	$Y_2O_3+Nb_2O_5+CaO$ (x=0.2)
	YNS-3	$Y_2O_3+Nb_2O_5+SrO$	YNC-3	$Y_2O_3+Nb_2O_5+CaO$

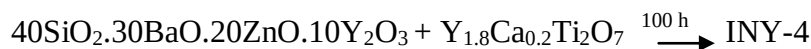
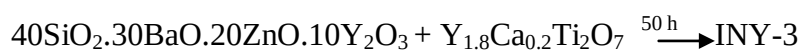
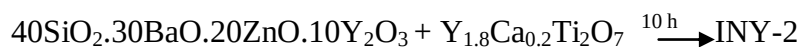
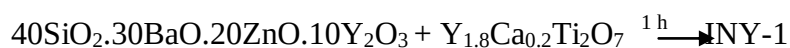
		(x=0.3)		(x=0.3)
	YNS-4	$Y_2O_3+Nb_2O_5+SrO$ (x=0.4)	YNC-4	$Y_2O_3+Nb_2O_5+CaO$ (x=0.4)
La_{1-x}M_xNbO_y (M= Sr, Ca)	LNS-1	$La_2O_3+Nb_2O_5+SrO$ (x=0.1)	LNC-1	$La_2O_3+Nb_2O_5+CaO$ (x=0.1)
	LNS-2	$La_2O_3+Nb_2O_5+SrO$ (x=0.2)	LNC-2	$La_2O_3+Nb_2O_5+CaO$ (x=0.2)
	LNS-3	$La_2O_3+Nb_2O_5+SrO$ (x=0.3)	LNC-3	$La_2O_3+Nb_2O_5+CaO$ (x=0.3)
	LNS-4	$La_2O_3+Nb_2O_5+SrO$ (x=0.4)	LNC-4	$La_2O_3+Nb_2O_5+CaO$ (x=0.4)

3.2.1 Powder preparation

Powders consisting of $Y_{1-x}M_xTiO_y$, $La_{1-x}M_xTiO_y$, $Y_{1-x}M_xNbO_y$ and $La_{1-x}M_xNbO_y$ system with M= Sr, Ca where x=0.1, 0.2, 0.3 and 0.4 were prepared. Moreover, in strontium-doped and undoped yttrium titanate ($Y_{1-x}Sr_xTiO_y$) system additional composition with x=0.025, 0.05, 0.075 were also prepared. The powder of each system was taken in appropriate stoichiometric amount. The purity of the oxides was greater than 99.9%. For all the above mentioned systems, composition x = 0.1, 0.2, 0.3 and 0.4 was selected. These oxides were first ground in agate mortar pestle in wet medium (acetone) for 1h to break any large agglomerates. The hand ground powders are further ball milled for 3h to reduce the particle size. The ball milling was done using porcelain balls in porcelain jar (Retsch, Germany, Model S 1000). The mass to ball ratio for each system was 1:2 which was kept constant for each milling. The resulting mixture was dried in air,

ground thoroughly to homogenize it and then calcined at different temperatures in alumina crucibles for 12 h in high temperature resistance furnace in air atmosphere (Bysakh & company, India). Before calcination, the furnace was calibrated by chromel alumel thermocouple and calcination was done in hot zone where fluctuation in temperature was ± 2 °C.

In addition to this, the interaction study was done between glass composition $40\text{SiO}_2.30\text{BaO}.20\text{ZnO}.10\text{Y}_2\text{O}_3$ and electrolyte $(\text{Y}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_{7-x}$ for $x=0.1$. The electrolyte was synthesized by taking oxides of Y_2O_3 , CaO and TiO_2 (Sigma Aldrich) in appropriate stoichiometric amount. The purity of the oxides was greater than 99.9%. These oxides were ball-milled for 5 h. The ground mixture was calcined at 1000°C for 12 h. The calcined powders were pressed into 20 mm diameter pellets of 1.5-2 mm thickness by applying ten tones pressure. The green pellets of $\text{Y}_{1-x}\text{Ca}_x\text{TiO}_y$ system with $x=0.1$ was sintered at 1550°C with a heating rate of 5°C min^{-1} for 12 h. Similarly $40\text{SiO}_2.30\text{BaO}.20\text{ZnO}.10\text{Y}_2\text{O}_3$ glass was prepared by taking an appropriate mole fraction of initial ingredients i.e., SiO_2 (99% CDH), BaCO_3 (99%, Sdfine), ZnO (99.5%, Sdfine), Y_2O_3 (99.995%, Sigma Aldrich). After grinding in mortar and pestle, the mixture was further transformed to ball mill and grinded for 2 h in wet medium (acetone). The ground powder was melted at 1550°C using intermediate stages of heating to facilitate calcinations and homogenization. For interaction study powders of glass and $(\text{Y}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_{7-x}$ for $x=0.1$ were mixed in 3:1 ratio by weight and heated at 1000°C for 1 h, 10 h, 50 h and 100 h as given below and the resultant products were characterized subsequently.



3.2.2 Pellets preparation

The calcined powders were crushed again and the powders with composition $Y_{1-x}M_xTiO_y$ and $Y_{1-x}M_xNbO_y$ (M=Sr, Ca) with $x=0.1, 0.2, 0.3, 0.4$ and $x=0.025, 0.05$ and 0.075 for $Y_{1-x}Sr_xTiO_y$ system were pressed into 20 mm diameter pellets of 1.5-2 mm thickness. Whereas, calcined powders with composition $La_{1-x}M_xTiO_y$ and $La_{1-x}M_xNbO_y$ (M=Sr, Ca) with $x=0.1, 0.2, 0.3, 0.4$ were mixed with 10 mole percent polyvinyl alcohol (PVA). Known weight of dried powders was transferred in a die which was manufactured from hardened die steel by Central Institute of Hand Tools, Jalandhar, Punjab (India). The die along with punch was kept below hydraulic press and a compaction pressure of 10 tones was applied slowly. After waiting for 1 minute, the pressure was released. Afterward the compacted mass was taken out. Moreover, some of the oxides of some selected samples were ground in agate mortar pestle for 1 h. The ground powders were pressed into 20 mm diameter pellets of 1.5-2 mm thickness by applying 10 tones pressure.

3.2.3 Sintering

The green pellets were sintered at 1550 °C for 12 h in air in a calibrated high temperature resistance furnace as shown in figure 3.1. Some selected samples were also sintered at different sintering temperature (1300-1400° C) to optimize the processing condition for achieving better properties. In other words, green pellets of $Y_{1-x}Sr_xTiO_y$ system with $x= 0, 0.025, 0.05, 0.075, 0.1, 0.2, 0.3, 0.4$, $Y_{1-x}Ca_xTiO_y$ system with $x=0.1$ was sintered at 1550° C and $x= 0.2, 0.3$ and 0.4 were sintered at 1500° C with a heating rate of $5^{\circ}C\ min^{-1}$ for 12 hours.



Figure 3.1: High temperature resistance furnace.

On the other hand, doped samples $\text{La}_{1-x}\text{Sr}_x\text{NbO}_y$ ($x = 0.1, 0.2, 0.3, 0.4$), $\text{La}_{1-x}\text{Ca}_x\text{NbO}_y$ ($x = 0.1, 0.2, 0.3, 0.4$) were sintered at $1300\text{ }^\circ\text{C}$ and $\text{Y}_{1-x}\text{Sr}_x\text{NbO}_y$ ($x = 0.1, 0.2, 0.3, 0.4$), $\text{Y}_{1-x}\text{Ca}_x\text{NbO}_y$ ($x = 0.1, 0.2, 0.3, 0.4$) were sintered at $1400\text{ }^\circ\text{C}$, respectively with a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ for 12 h. The flow chart of the experimental procedure is shown in figure 3.2. In addition to this, two different routes of solid state reaction method were followed to synthesize selected samples. In the first process, pellets were sintered directly up to $1550\text{ }^\circ\text{C}$ without any intermediate holding time with a fast heating rate of $7\text{ }^\circ\text{C min}^{-1}$ and holding at $1550\text{ }^\circ\text{C}$ for 12 h. Whereas, in the second process, holding time of 30 min at $400\text{ }^\circ\text{C}$, $800\text{ }^\circ\text{C}$, $1200\text{ }^\circ\text{C}$ and 12h at $1550\text{ }^\circ\text{C}$ was given with slow heating rate of $2\text{ }^\circ\text{C min}^{-1}$. Moreover, one set of green pellets of some selected samples were sintered at $1500\text{ }^\circ\text{C}$ with a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ for 12 h and another set of green pellets were sintered at $1550\text{ }^\circ\text{C}$ for 12 h in order to study the effect of processing conditions on various properties of $\text{Y}_2\text{Ti}_2\text{O}_7$.

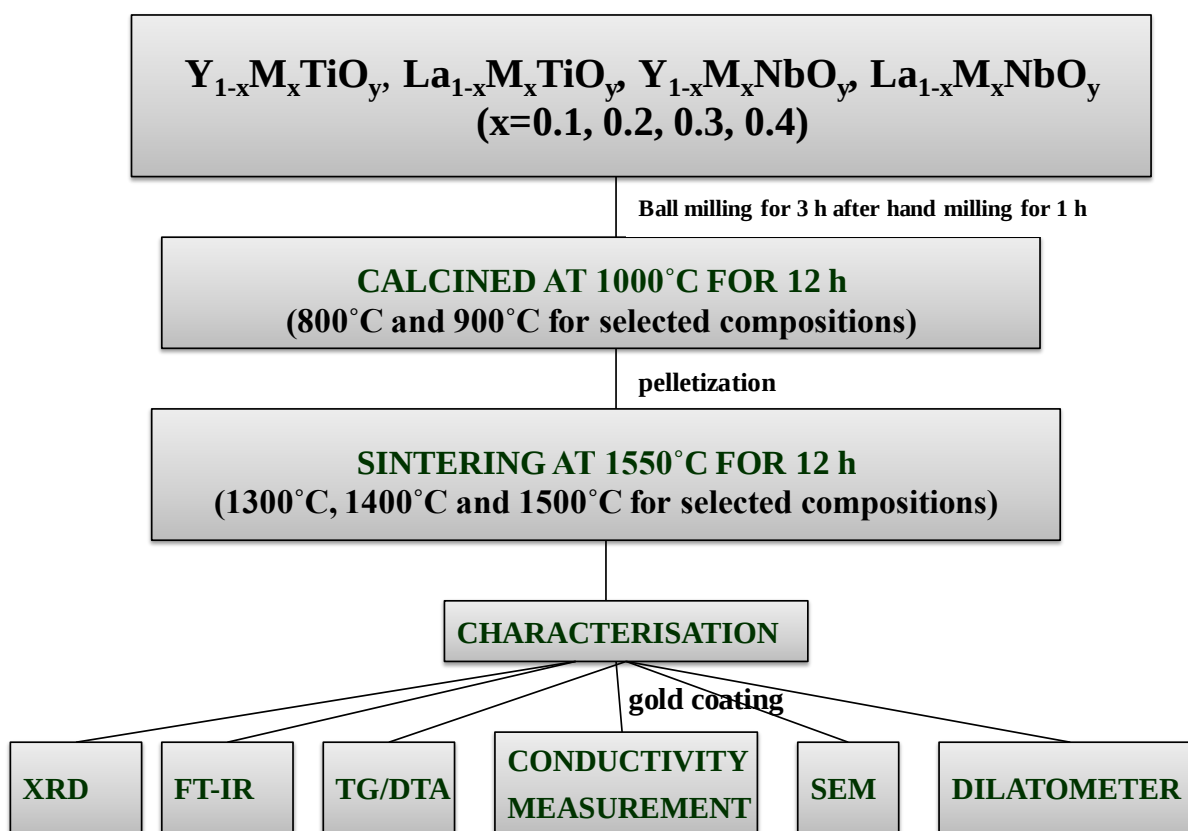


Figure 3.2: Flow chart of experimental procedure.

3.3 Characterization of materials

The sintered samples were further characterized in-order to determine the structure, conductivity measurement and thermal analysis. For the analysis of above parameters, the sintered samples were characterized using X-ray diffraction (XRD), thermo gravimetric analysis (TG)/differential thermal analysis (DTA), Fourier transform infra-red spectroscopy (FT-IR), scanning electron microscopy (SEM), Energy dispersive spectroscopy (EDS) and Electron paramagnetic resonance (EPR). Conductivity was measured by ac - impedance spectroscopy technique and band gap by UV visible spectroscopy. The details of these techniques are given below:

3.3.1 X-Ray diffraction

X-ray diffraction is one powerful technique to obtain crystallographic information about a sample. When an electron moving at high speed is directed to a metal target, then a small percentage of their kinetic energy is converted into X-rays. The Bragg condition for reflection of X-rays by the atomic planes is given by:

$$2d \sin \theta = n \lambda \quad (3.1)$$

where d = interplanar spacing; λ = wavelength of incident x-ray,
 θ = diffraction angle, n = integer

The lattice parameters (a , b , c) were calculated with interplanar spacing d as follows:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad (\text{cubic}) \quad (3.2)$$

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (\text{orthorhombic}) \quad (3.3)$$

where h , k and l are miller indices.

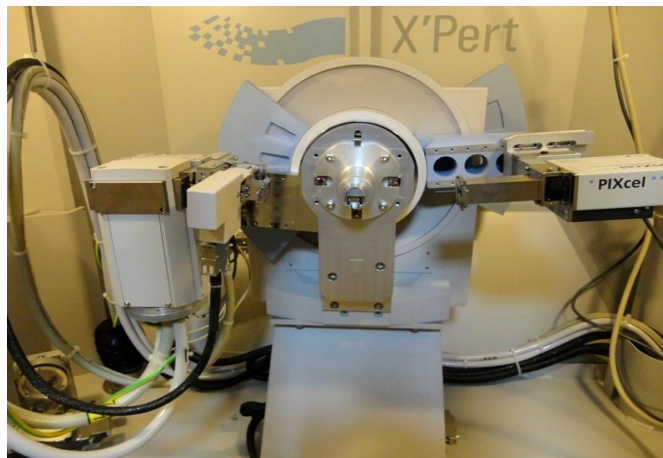


Figure 3.3: X-ray diffractometer (XRD).

The X-ray diffraction study of the sintered samples was done to identify crystalline phases. The X-ray diffraction of the samples were performed using Rigaku model Geiger diffractogram with CuK_α radiation ($1.5418\text{\AA}$) obtained from copper target using an in-built Ni filter. During XRD experiment, scan speed was 5° /minute. In addition to this, X-ray diffraction of some of the samples was performed using XPert PanAnalytical with CuK_α radiation (figure 3.3). The volume fraction of different crystalline phases was calculated using full-score software which is attached with the instrument. The diffraction data of the samples was indexed using standard powder diffraction files provided by International Centre for Diffraction Data -ICDD (formally known as JCPDS).

3.3.2 Thermal gravimetric (TG)/ Differential thermal analysis (DTA)

Thermogravimetry (TG) measures the change in sample mass with temperature by using a thermo-balance. Thermal gravimetric analysis (TGA) was done to find out the mass change due to decomposition of phases and thermal stability of the samples. Differential thermal analysis (DTA) is a technique that determines the difference in temperature between the sample and an inert reference material as a function of temperature. The temperature of the sample and reference are same until some thermal event occurs in the sample. In this manner, the temperature can be found at which any event either absorbs or release heat occurs. The sample temperature either leads (if the change is exothermic) or lags behind (if the change is endothermic). These changes are attributed to phase transition, order-disorder transitions and chemical reactions. The present samples were analyzed by both TG and DTA techniques. The TG/DTA experiment was done with heating rate of $10^\circ\text{C}/\text{min}$ from room temperature to 1000°C in N_2 atmosphere by Perkin Elmer (Model: Pyris Diamond). Whereas, TG/DTA experiment for

selected samples was also done in argon and air atmosphere. Analysis of all the samples was performed by taking alumina as reference sample.

3.3.3 Scanning electron microscopy (SEM)

Scanning electron microscope (SEM) plays an important role for the analysis of rough as well as smooth surfaces. The SEM images provide the information regarding grain size, shape, porosity and agglomeration of the powder (figure 3.4). SEM exhibits properties of high resolution, extensive magnification range and high depth of field. The sample for SEM analysis is mounted on a conductive substrate such as aluminum stub and gold plated in vacuum. The gold coated samples were kept at the sample stage of the microscope. The sample can be moved in X, Y and Z directions, tilted as well as rotated. Further, the data signal is released due to interaction between bombarding electrons and atoms of the specimen. These data signal arise due to elastic or inelastic collisions of beam electrons with the atoms of the specimen. The elastic (electron-nucleus) collisions produces back scattered electrons (BSE) and inelastic (electron-electron) produces secondary electrons. The back scattered electrons provides topographic as well as compositional information about the specimen. In other words, SEM micrographs could be taken in two modes i.e., secondary emission and back scattered. In the present investigation secondary emission mode was used. In the present study, the SEM was done using JEOL JSM-6510 LV equipment to support the XRD and conductivity results. Grain sizes were also measured directly from the micrographs of the samples.



Figure 3.4: Scanning electron microscope (SEM).

3.3.4 Fourier transform infra-red spectroscopy (FT-IR)

Infra-red spectroscopy is used to measure the vibrational frequencies of bonds in the molecule. The IR scans a range of different frequencies (in the infrared part of the electromagnetic spectrum) and frequency that matches with the characteristic frequency of a bond gets absorbed. The characteristic vibrational frequency of bonds depends on the masses of the atoms in the bond and strength of the bond. Fourier-Transform Infra-red spectrophotometer uses an interferogram and polychromatic light to generate an interferogram. The interferogram is then mathematically decoded by a Fourier transform. FT-IR spectrometers are fast, easy to use and provide accurate results compared to other types of spectrometers.

In the present study, Fourier-Transform Infra-red spectroscopy (FT-IR) was done at room temperature using a Perkin Elmer Spectrum BX2. The powder samples and KBr were mixed in

1:100 ratios respectively. The mixture was pressed in the form of pellet of 13 mm diameter for FT-IR measurement.

3.3.5 Conductivity measurement

Ion motion in disordered solids is different from electronic conduction in crystalline solids. Ions are much heavier than electrons and ionic motion can be described by hopping between charge compensating sites. The materials that conduct ions are known as solid electrolytes which are commonly used in many different applications. The ionic migration proceeds via defects, either vacancies or interstitial, and the structure should therefore exhibit a high level of disorder. In addition to this, the ionic conduction can be accompanied with electronic conduction. Impedance spectroscopy is a technique used to analyze the electrical response of polycrystalline sample in a wide range of frequencies at different temperatures [1]. SOFC electrolytes are oxygen ion conductors and can therefore be studied using this technique of impedance spectroscopy. The ac electrical conductivity is obtained using the relation:

$$\sigma_{ac} = l/SZ \quad (3.4)$$

where l is the thickness and S is surface area of the sample. It is observed that at low temperatures, σ_{ac} varies linearly with frequency. This is due to the fact that the frequency variation of σ_{ac} involves a power exponent ($\sigma_{ac} \propto \omega^n$, n is the exponent and ω is the angular frequency of ac field). On the other hand, at higher temperature, frequency independent ac conductivity is observed in low frequency region. This frequency independent region increases with increasing temperature and obeys the relation [2]:

$$\sigma_{ac} = \sigma_{dc} + A\omega^n \quad (3.5)$$

with $0 \leq n \leq 1$, A is thermally activated quantity and σ_{dc} is frequency independent part of conductivity. In addition to above, it is observed that in case of ac conductivity, high frequency parts of ac conductivity are governed by ion movements in the bulk of the solid electrolyte, while the low frequency part is governed by electrode polarization. Since the ions are blocked by the metal electrode, there is accumulation of ions near the electrodes resulting in the drop in voltage and development of electrical polarization of the material [3]. Therefore, ac conductivity decreases with decrease in frequency. Moreover, the nature of variation of ac conductivity in the high temperature region obeys the Arrhenius relationship:

$$\sigma_{ac} = \sigma_0 \exp(-E_a/k_B T) \quad (3.6)$$

where E_a is the activation energy of conduction and T is the absolute temperature. The increase in conductivity with temperature can be explained on the basis of oxygen vacancies created due to loss of oxygen within the bulk during sintering process. The charge compensation follows the reaction by Kroger and Vink notation [4]:



which results in generation of electrons. In the present study, gold sputtered pellets were used to carry out ac conductivity measurements in the temperature range of 100-900°C. The coating unit used for sputtering is shown in figure 3.5. The two probe ac conductivity measurement was done using an ac impedance spectroscopy with Model 4274A multi-frequency Hewlett-Packard LCR meter (figure 3.6) in the frequency range of 100 Hz-100 KHz.

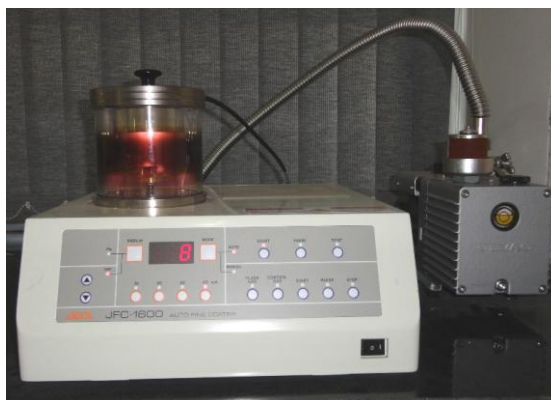


Figure 3.5: Coating unit for sputtering of pellets.



Figure 3.6: LCR meter for ac conductivity measurement along with furnace.

3.3.6 Dilatometric measurement

The dilatometer is used to determine the Thermal Expansion coefficient (TEC), softening point, glass transition temperature, curie point, phase transition, shrinkage and stress relaxation. In the present work, dilatometry of the sintered samples was done by dilatometer, Netzsch (DIL 402 PC) in air using alumina kit including alumina push rod at a heating rate of 5°C/min from room temperature to 1000 °C. Thermographs has been taken between temperature and percentage change in length of the sample. Thermal expansion coefficient of all the samples was measured from room temperature to 1000 °C.

3.3.7 Electron paramagnetic resonance (EPR)

The electron spin resonance (ESR) is a technique to determine frequency and magnetic moment of an electron in a given magnetic field. Since, one large group of solids i.e., group of paramagnetic materials show resonance so ESR in these materials are often called electron paramagnetic resonance (EPR). One major requirement for the existence of electron spin resonance is that the ions or atoms should not have completely filled shells. In completely filled shells, the electrons are paired and such shells have no net spin. In the present study, Electron paramagnetic resonance spectra (X-band) was recorded with EMX- Biospin, Bruker, A 300; USA operating at X-band frequency at room temperature.

3.3.8 UV visible spectroscopy

Ultraviolet visible spectroscopy is used to obtain the absorbance spectra of a compound in solution or as a solid. UV visible spectroscopic data can give qualitative and quantitative information of a given compound or molecule. Atoms and molecules exist in several defined energy states or levels and a change of level requires the absorption or emission of an integral number of a unit of energy called a quantum or a photon. The energy of a photon absorbed or emitted during a transition from one molecular energy level to another is given by

$$E = hc/\lambda \quad (3.8)$$

Where h is known as Planck's constant. A molecule of any substance has an internal energy equal to the sum of the energy of its electrons, the energy of vibration between its constituent atoms and the energy associated with rotation of the molecule. The electronic energy levels of simple molecules are widely separated and absorption of very high energy photon results in excitation of a molecule from one level to another. Whereas in case of the complex molecule energy levels are more closely spaced and photons of near ultraviolet and visible light can effect

the transition. These substances can therefore absorb light in some areas of near ultraviolet and visible regions. For ultraviolet wavelength, the absorption spectrum of a molecule shows very sharp lines. Each line occurs at a wavelength where the energy of an incident photon exactly matches with the energy required to excite an electronic transition. However, in practice the ultraviolet spectrum of most molecules consist of few humps rather than sharp lines. These humps show that the molecule is absorbing radiation over a band of wavelengths. These bands occur due to electronic level transitions which are accompanied by simultaneous change between numerous vibrational levels.

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RESULTS AND DISCUSSION

Overview

In this chapter, the experimental results of different compositions are presented. The entire work has been done to achieve the properties of materials which make them suitable as components for solid oxide fuel cell (SOFC). This chapter deals with the study on systematic doping of Sr^{2+} and Ca^{2+} for Y^{3+} in $\text{Y}_{1-x}\text{M}_x\text{TiO}_y$ ($\text{M}=\text{Ca}, \text{Sr}$) system, La^{3+} in $\text{La}_{1-x}\text{M}_x\text{TiO}_y$ ($\text{M}=\text{Ca}, \text{Sr}$) system, Y^{3+} in $\text{Y}_{1-x}\text{M}_x\text{NbO}_y$ ($\text{M}=\text{Ca}, \text{Sr}$) system and La^{3+} in $\text{La}_{1-x}\text{M}_x\text{NbO}_y$ system with $x=0, 0.1, 0.2, 0.3, 0.4$ was chosen to find the solid solubility limit and its effect on conductivity. The results are discussed in light of oxygen vacancies, order and disorder transitions using electrical conductivity, X-ray analysis, FT-IR, TGA, TEC and SEM in-order to check its suitability for SOFC.

4.1 Synthesis of $Y_{1-x}M_xTiO_y$ ($0.1 \leq x \leq 0.4$); $M = Sr, Ca$ systems:

Perovskite (ABO_3) and pyrochlore ($A_2B_2O_7$) compounds are inherent ionic conductors whose properties can be altered by changing the processing conditions and substitution of different elements on A and B sites. These materials can also be used as solid electrolyte in solid oxide fuel cell [1]. In the present work, oxides of Y_2O_3 and Ti_2O_3 were taken in appropriate stoichiometric amount and sintered at two different temperatures (1500 °C and 1550 °C) for 12 h. The as prepared samples hereafter are called YT-1 and YT-2 respectively. The oxides of Ti_2O_3 and TiO_2 were taken to study the phase formation, phase transformation and their properties. The selection of two different ingredients of Ti is based on their different chemical properties. For instance, it is expected that Ti^{3+} in Ti_2O_3 might be partially converted into Ti^{4+} state during sintering and may lead to mixed titanium states (Ti^{3+} , Ti^{4+}) in different crystalline structure leading to different properties. Moreover, the lattice energy of Ti_2O_3 is more as compared to TiO_2 . Based on these assumptions, yttrium titanate ($Y_2Ti_2O_7$) was synthesized by solid state reaction method. On the other hand, oxides of Y_2O_3 and TiO_2 were taken in appropriate stoichiometric amount and two different routes of solid state reaction method were followed to synthesize other samples. In first method, pellets were sintered directly up to 1550 °C without any intermediate holding time with a fast heating rate of 7 °C min⁻¹ and holding at 1550 °C for 12 h. Whereas, in the second process, holding time of 30 min at 400 °C, 800 °C, 1200 °C and 12 h at 1550 °C was given with slow heating rate of 2 °C min⁻¹. The sample prepared by first process was named as Y-1 and sample prepared by second process was named as Y-2. In addition to this, the effect of systematic doping of SrO and CaO for Y_2O_3 in $Y_2Ti_2O_7$ system was also investigated. Therefore, different Sr-doped and Ca-doped $Y_2Ti_2O_7$ system i.e., $Y_{1-x}M_xTO_y$ ($M = Sr$

or Ca; T=Ti) system ($x=0, 0.1, 0.2, 0.3, 0.4$) was synthesized by solid state reaction technique and described in the subsequent sections.

4.1.1 Density measurement

In order to study the effect of sintering temperature on density, both the samples i.e., YT-1 and YT-2 were sintered at different temperature and duration. Theoretical density was calculated using experimental lattice parameters and chemical formula of $Y_2Ti_2O_7$ and $YTiO_{2.085}$ phases which were confirmed by XRD analysis and discussed later. The variation of relative densities with respect to temperature of samples YT-1 and YT-2 are given in figure 4.1.

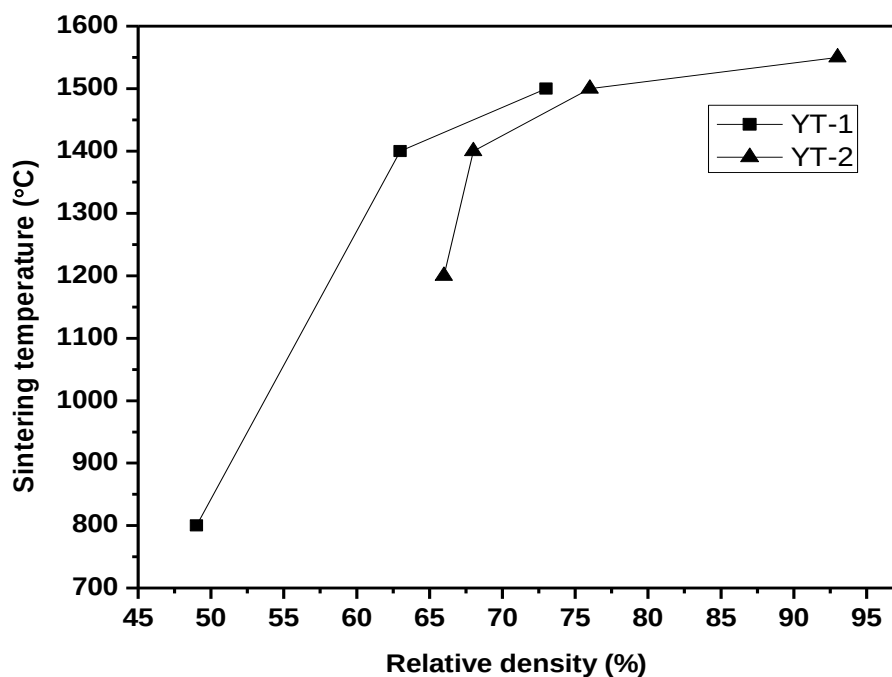


Figure 4.1: Relative densities of YT-1 and YT-2 samples sintered at various temperatures for holding time of 12h.

It is observed that relative density of YT-2 sample comes to be approximately 94%. However, the relative density of YT-1 sample is lower than YT-2 sample. The lower density of YT-1 sample might be attributed due to presence of secondary minor phase as indicated in XRD of this

sample. In general, pyrochlore showed poor sintering characteristics as reported in case of $\text{Gd}_2\text{Ti}_2\text{O}_7$ phase [2]. The density of $\text{Gd}_2\text{Ti}_2\text{O}_7$ is dependent on sintering temperature and holding time.

On the other hand, some Sr doped samples show good sinterability at 1550 °C and density obtained is more than 90% of the theoretical density except YST-4 sample as has been reported for $\text{Gd}_2\text{Ti}_2\text{O}_7$ system [3, 4]. It was found that YST-2 sample exhibits lower density than YST and YST-1 samples. The decrease in density of YST-2 sample seems to be related with the formation of SrTiO_3 phase which is less dense than pyrochlore phase. It is well reported in literature that the grain growth of SrTiO_3 is very sensitive of local environment [3, 5-7]. Moreover, the decrease in density of YST-4 sample seems to be related with increase in grain growth of the sample as shown in figure 4.17 (e) (discussed later). The relative density of Ca doped samples is found to be greater than 90% as summarized in table 4.1. As observed from the table 4.1, YCT-2, YCT-3 and YCT-4 samples exhibits lower density than YCT-1 sample. The decrease in densities of these samples in comparison with YCT-1 sample seems to be related with porosity as observed in SEM micrographs of these samples.

Table 4.1: Relative densities of YST, YST-1 to YST-4, YCT-1 to YCT-4 samples.

Sample Name	YST	YST-1	YST-2	YST-3	YST-4	YCT-1	YCT-2	YCT-3	YCT-4
Relative Density (%)	93	94	92	95	85	93	92	91	87

4.1.2 X-ray diffraction analysis (XRD)

X-ray diffraction pattern of YT-1 sample shows the formation of two phases namely $\text{Y}_2\text{Ti}_2\text{O}_7$ (ICDD Card No. = 01-085-1584) and $\text{YTiO}_{2.085}$ (ICDD Card No. = 01-085-0001) as shown in figure 4.2. The volume fraction of $\text{Y}_2\text{Ti}_2\text{O}_7$ phase is higher as compared to $\text{YTiO}_{2.085}$ phase.

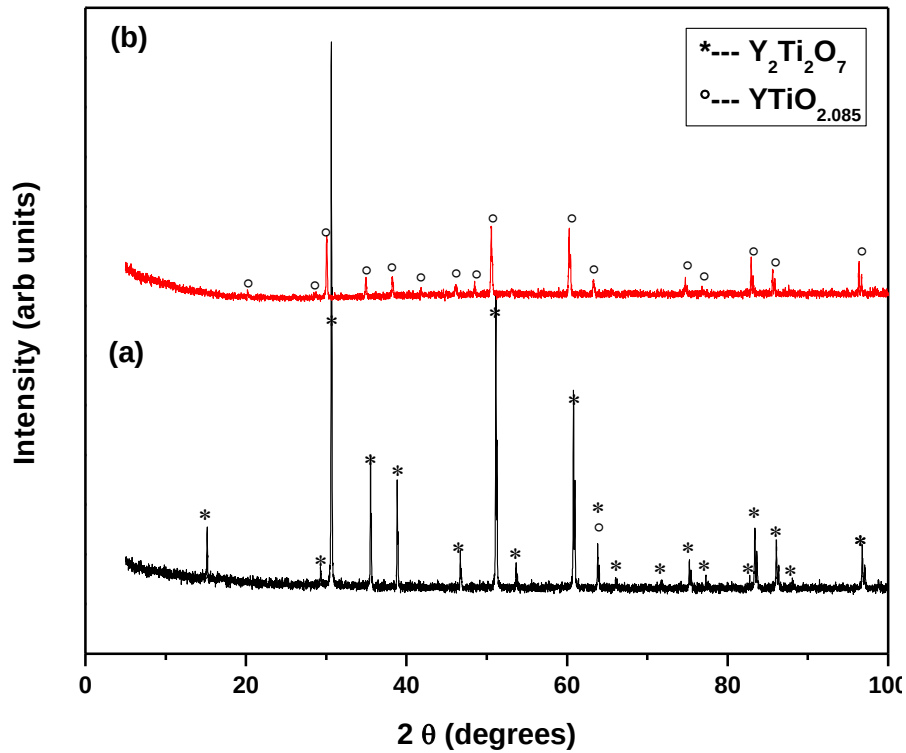


Figure 4.2: X-ray diffraction pattern of (a) YT-1 (b) YT-2.

As the heat treatment temperature of the sample is increased from 1500 °C to 1550 °C for the same time period (12h), the volume fraction of $\text{YTiO}_{2.085}$ phase increases drastically and sample becomes almost monophasic. Apart from this, the XRD peaks of this phase shift towards lower angle as compared to reported phase (ICDD Card No. = 01-085-0001). The lower angle shifting in XRD indicates the presence of tensile strain in the sample. Moreover, the full width at half maximum (FWHM) also decreases with increase in sintering temperature. Based on X-ray diffraction pattern, the lattice parameters of both the phases were calculated as $a = 10.06$ and $10.16 \text{ \AA}$ for YT-1 and YT-2, respectively. The lattice parameter of YT-2 sample is slightly higher than YT-1 sample. It might be attributed due to higher content of oxygen vacancies in YT-2 sample which might have caused some distortion in ideal cubic lattice of pyrochlore

structure [2]. Additionally, the transformation of Ti^{3+} to Ti^{4+} might decrease volume of unit cell due to size difference in Ti^{4+} and Ti^{3+} cations. The presence of mixed state of titanium i.e., Ti^{3+} and Ti^{4+} are further confirmed by the EPR measurement. The EPR spectra of both the samples are depicted in figure 4.3. It is well reported in the literature that the intensity of the spectra increases with increasing unpaired electrons in compound. In general, higher ratios of $\text{Ti}^{3+}/\text{Ti}^{4+}$ lead to higher intensity of the EPR spectra [8, 9]. In the present samples, the stronger spectra is obtained in case of YT-2 sample which indicates that $\text{Ti}^{3+}/\text{Ti}^{4+}$ ratio is higher in YT-2 sample as compared to YT-1 sample.

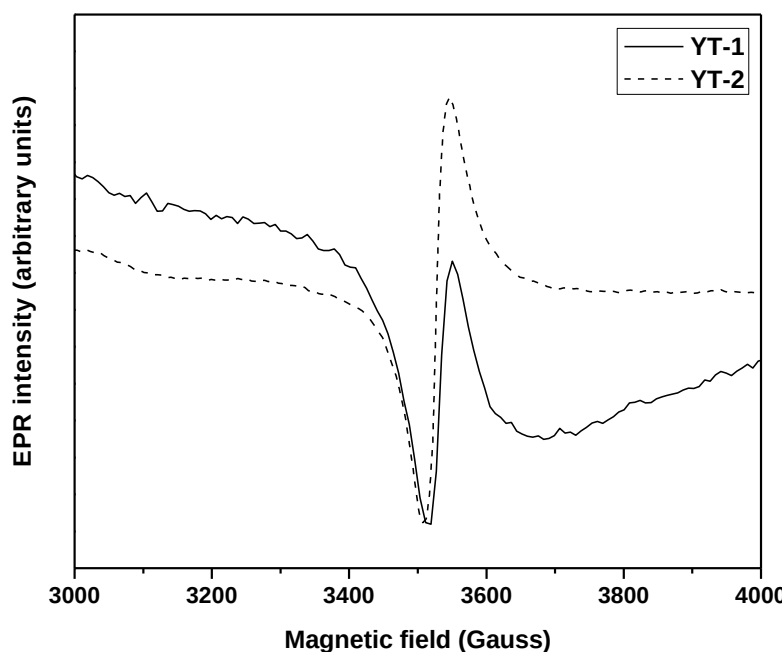


Figure 4.3: EPR spectra of YT-1 and YT-2 samples.

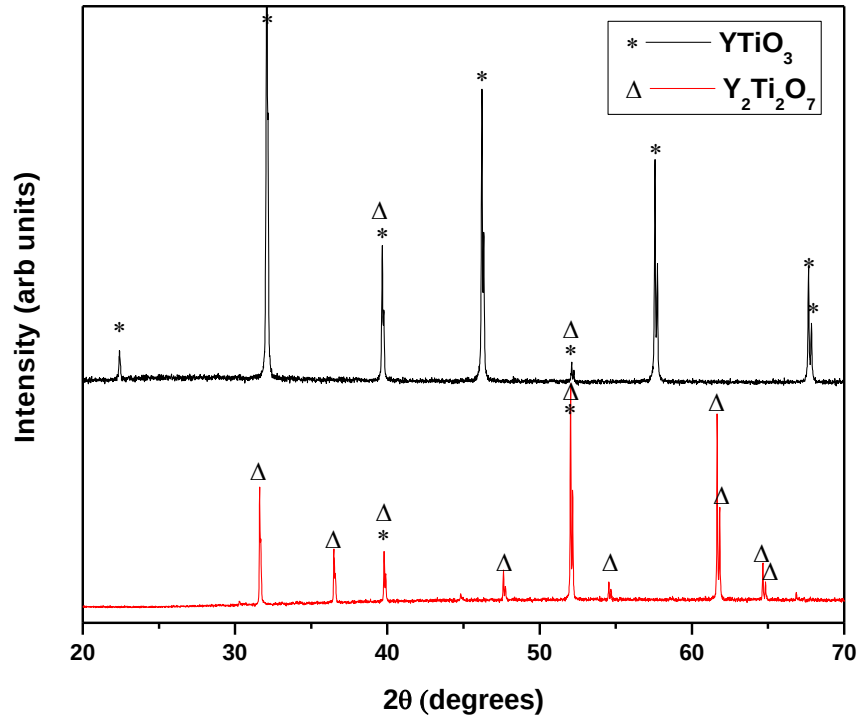


Figure 4.4: X-ray diffraction of Y-1 and Y-2 sample.

XRD patterns of Y-1 and Y-2 samples are shown in the figure 4.4. X-ray diffraction pattern of Y-1 sample shows the formation of orthorhombic YTiO_3 phase with space group Pbnm [10] (ICDD Card No. = 01-073-0071). The Goldschmidt tolerance factor G_t in YT-1 sample comes out to be 0.8455 i.e., lesser than unity indicating that structure is not cubic [11]. On the other hand, Y-2 sample exhibits cubic $\text{Y}_2\text{Ti}_2\text{O}_7$ phase (ICDD Card No. = 01-073-1697). However, in both the cases, the initial ingredients and amount of Y_2O_3 and TiO_2 was same. It is clear from XRD analysis that the slow heating processing condition and lower particle size (ball milled) sample plays a significant role to prevent the conversion of Ti^{4+} to Ti^{3+} at the higher temperature sintering (1550°C). In contrast to this, the fast heating rate with no intermediate holding leads to the formation of perovskite phase (YTiO_3). It is quite possible that the Ti^{4+} reduces to Ti^{3+} state due to creation of reducing atmosphere at that temperature during sintering [12]. In addition to

this, the sintered Y-2 sample appeared to be dark yellow in color which is reported to be the stable state of the TiO_2 based systems [13]. Contrary to this, the fast heated sample appeared to be grey in color which is clear indication of reduction of Ti^{4+} to Ti^{3+} with higher oxygen vacancies [12]. During the reduction process, there are possibilities of either formation of oxygen vacancies or Ti occupying the interstitial sites that depends on the annealing temperature [12]. Similar results have also been reported by Ramesha et al., [14] for $\text{Pb}_2\text{MnReO}_6$ systems.

In addition to this, XRD of Sr doped samples i.e., YST, YST-0.025, YST-0.05, YST-0.075, YST-1, YST-2, YST-3 and YST-4 samples are shown in the figure 4.5 (a) and (b). Moreover, $\text{Y}_{1-x}\text{M}_x\text{TiO}_y$ ($\text{M}=\text{Ca}$; $\text{T}=\text{Ti}$) system with $x=0.1, 0.2, 0.3, 0.4$ comprises of four samples.

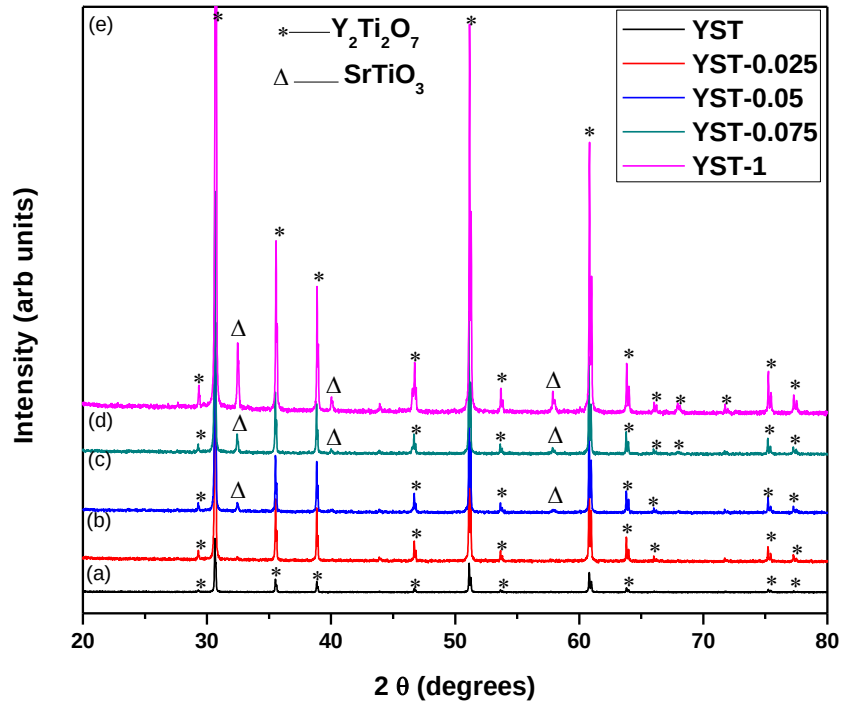


Figure 4.5(a): X-ray diffraction patterns of (a) YST, (b) YST-0.025, (c) YST-0.05, (d) YST-0.075 and (e) YST-1.

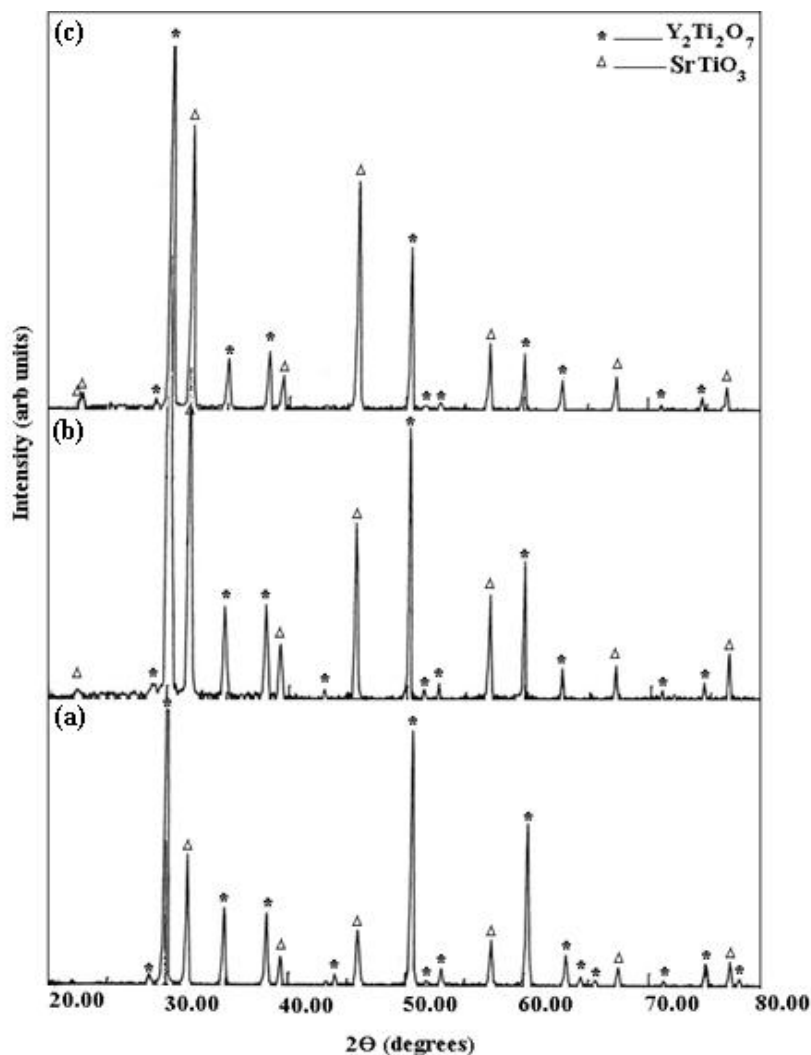


Figure 4.5(b): X-ray diffraction patterns of (a) YST-2, (b) YST-3 and (c) YST-4.

X-ray diffraction pattern of YST and YST-1 samples shows the formation of $\text{Y}_2\text{Ti}_2\text{O}_7$ (ICDD Card No. = 73-1697). All the XRD peaks are indexed with cubic pyrochlore phase of space group $\text{Fd}3\text{m}$ [15]. However, in comparison to YST sample, YST-1 sample exhibits low intensity XRD peaks. It is clearly showing that the doping of Sr^{2+} might be working as sintering aid as the density of the sample increases as shown in table 4.1.

X-ray diffraction pattern of YST-0.025, YST-0.05 and YST-0.075 samples are shown in figure 4.5(a). Similar results have also been reported for high ionic radii dopants for different

pyrochlore systems [16]. On the other hand, the higher concentration of doping ($x = 0.05, 0.075, 0.1, 0.2, 0.3$ and 0.4) disrupt the $Y_2Ti_2O_7$ phase and leads to formation of $SrTiO_3$ minor phase. The XRD pattern of YST-0.05, YST-0.075, YST-1, YST-2 and YST-3 samples clearly shows the presence of $SrTiO_3$ secondary phase. However, in case of YST-0.05, a small kink at lower angle shows the nucleation of $SrTiO_3$ phase that has just started in case of YST-1 sample. As soon as Sr^{2+} increases above critical value, it induces the phase separation and form $SrTiO_3$ phase. This can be explained because of charge compensation. The substitution of Y^{3+} with cation of lower valence state (Sr^{2+}) causes an electronic unbalance in the pyrochlore lattice that can be compensated either with the generation of oxygen vacancy or change in B cationic site at higher oxidation state.

X-ray diffraction pattern of YCT-1 sample (figure 4.6) shows the formation of single phase of $Y_2Ti_2O_7$ (ICDD Card No. = 01-070-7909). The XRD pattern of YCT-2 and YCT-3 samples clearly shows the presence of $Y_2Ti_2O_7$ phase and orthorhombic $CaTiO_3$ phase (ICDD Card No. = 01-089-0056) whereas YCT-4 sample shows the presence of $Y_2Ti_2O_7$ phase and $CaTiO_3$ phase (ICDD Card No. = 01-075-0437), respectively. The doping of Ca^{2+} up to $x=0.1$ in present system, results in the formation of solid solution. In other words, the solubility limit of calcium in $Y_{1-x}Ca_xTiO_y$ system comes out to be nearly unity which is in agreement with the results reported by Eberman et al., [4]. Similar results have also been reported for doping of different pyrochlore systems [17]. The lattice parameter ($10.11 \text{ \AA}$) of YCT-1 sample clearly indicates the increment as compared to the pure sample. Obviously, the Ca^{2+} ($1.12 \text{ \AA}$) are larger than Y^{3+} ($1.02 \text{ \AA}$) and replacement of Y^{3+} leads to enhancement in the lattice parameter.

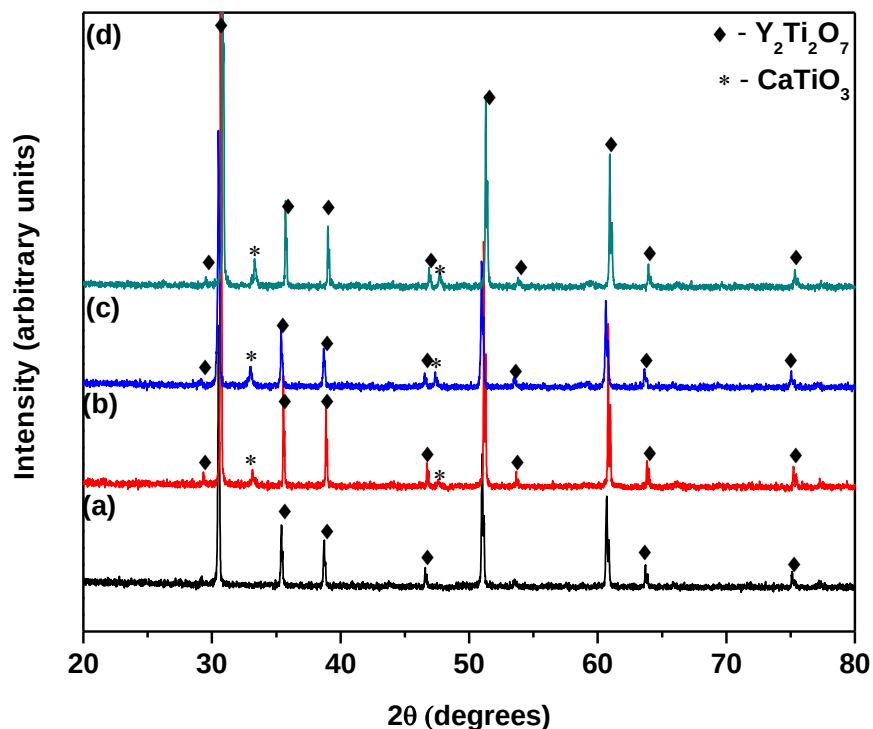


Figure 4.6: X-ray diffraction pattern of (a) YCT-1, (b) YCT-2, (c) YCT-3 and (d) YCT-4, samples.

On the other hand, the higher concentration of doping ($x = 0.2, 0.3$ and 0.4) disrupts the $\text{Y}_2\text{Ti}_2\text{O}_7$ phase and leads to formation of CaTiO_3 minor phase. In other words, as soon as Ca^{2+} concentration increases above the critical value, it induces the phase separation and form CaTiO_3 phase. This can be explained because of charge compensation. The substitution of Y^{3+} with cation of lower valence state (Ca^{2+}) causes an electronic unbalance in the pyrochlore lattice that can be compensated with the generation of oxygen vacancy up to certain doping concentration (solid solubility limit). Interestingly, higher doping concentration ($x = 0.4$) leads to deviate the orthorhombic to cubic crystal structure of CaTiO_3 . The volume fraction of $\text{Y}_2\text{Ti}_2\text{O}_7$ phase and CaTiO_3 phase in all the samples are indicated in figure 4.7.

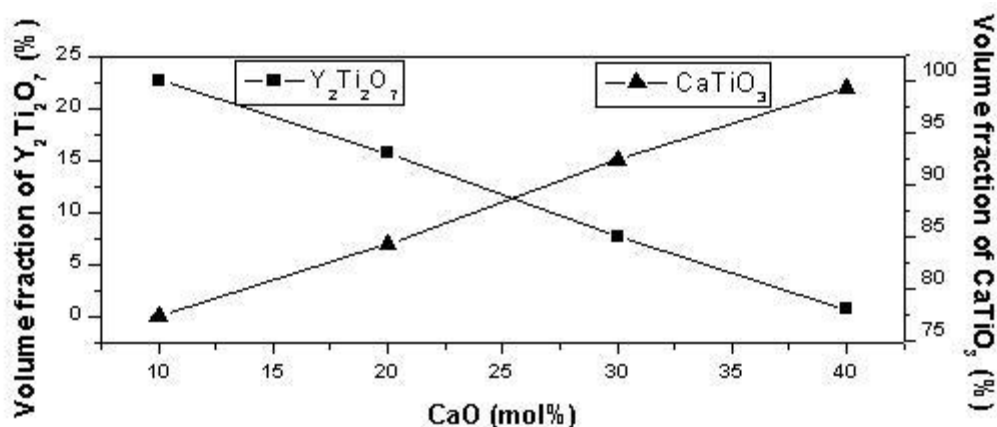


Figure 4.7: Volume fraction of $Y_2Ti_2O_7$ and $CaTiO_3$ phase for various concentration of calcium.

The volume fraction of perovskite ($CaTiO_3$) phase in $Y_2Ti_2O_7$ decreases with the increase of CaO mole %. The lattice parameters with dopant concentrations could not show any sequence. The nonlinearity in lattice parameter is in agreement with the previously reported values of Cr-substituted $Y_2Sn_2O_7$ system [18]. This type of anomalies in lattice parameters can be explained on the refinement of $\langle A-O \rangle$ bond distance and the cell parameters. Basically, $\langle A-O \rangle$ distance increases with increasing Cr^{4+} (0.56 Å) content up to threshold value (i.e. increasing cell parameter). However, bond length expansion reaches up to certain value after that it decreases. This might be possible because of existing exponential law relating to potential energy and interatomic distance of O-O edge [19]. On the other hand, the perovskite structured materials behave differently than pyrochlore systems. In fact, the variation in A and B distances tends to compensate each other [20]. Conclusively, the change in lattice parameters after solid solubility limit is very complex due to presence of secondary phase ($CaTiO_3$) for higher dopant concentration i.e., $x > 0.1$. In case of Y-1 sample, the value of lattice parameters decreases as compared to the reported lattice parameters of the same phase. It may be due to presence of titanium in mixed state instead of presence of only Ti^{3+} ions in Y-1 sample. The presence of Ti^{4+}

leads to shrinkage in the lattice parameter of this sample due to lower ionic radii of Ti^{4+} as compared to Ti^{3+} cations.

Table 4.2: Lattice parameters, calculated and reported values of Y-1 sample and Y-2 sample.

Sample Name	Phases obtained	Lattice Parameters (Å)		
		a	b	c
Y-1	YTiO_3	5.56 (C)*	5.52 (C)*	7.88 (C)*
		5.59 (R)*	5.59 (R)*	7.91 (R)*
Y-2	$\text{Y}_2\text{Ti}_2\text{O}_7$	10.16 (C)*	10.16 (C)*	10.16 (C)*
		10.09 (R)*	10.09 (R)*	10.09 (R)*

*C and R are calculated and reported values of lattice parameters respectively.

Conclusively, the sample is in compressive strain condition that can be easily seen and correlated with the SEM micrographs of Y-1 sample (detail discussion is given in SEM section). In addition to this, Williamson and Hall plot of Y-1 and Y-2 sample are shown in figure 4.8.

The strain is calculated from the slope of the fit whose value comes out to be 0.115 for Y-1 sample and 0.109 for Y-2 sample confirming that strain is higher in Y-1 sample in comparison to Y-2 sample. Similar analysis has also been done by Woodward et al., [21].

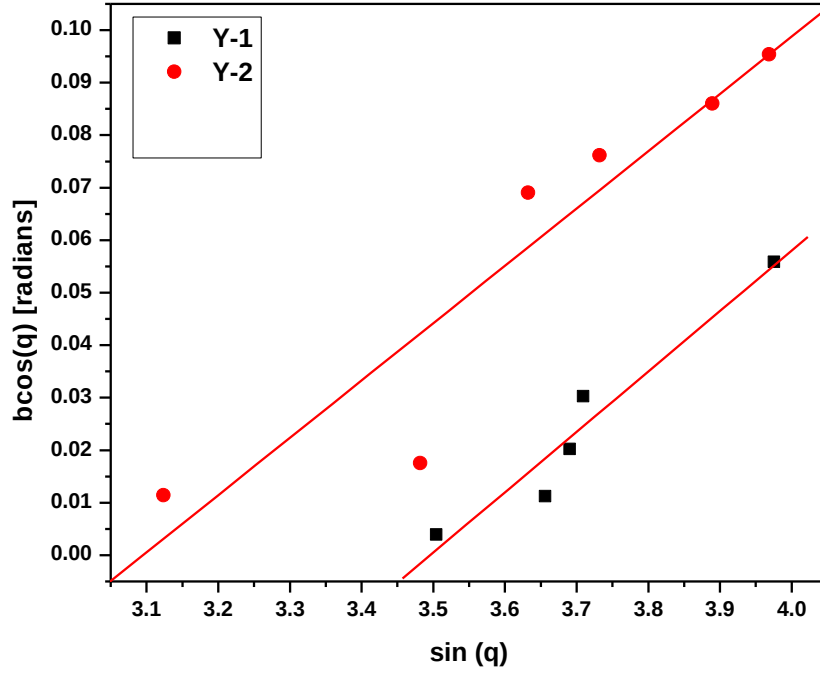


Figure 4.8: Williamson-Hall plots for the samples Y-1 and Y-2, respectively

On the other hand, Sr-doped samples may lead to higher oxidation state of transition element (Ti) leading to smaller ionic radii which may result in contraction of lattice parameter as observed in many doped perovskites [17, 22, 23]. The doping of Sr^{2+} ($1.26\text{\AA}$) leads to decrease in the lattice parameter in the present system. However, the size of dopant ($\text{Sr}^{2+} = 1.26\text{\AA}$) is larger than host ($\text{Y}^{3+} = 1.02\text{\AA}$). The lattice parameters are calculated for YST, YST-0.025, YST-0.05, YST-0.075, YST-1 samples and are shown in figure 4.9.

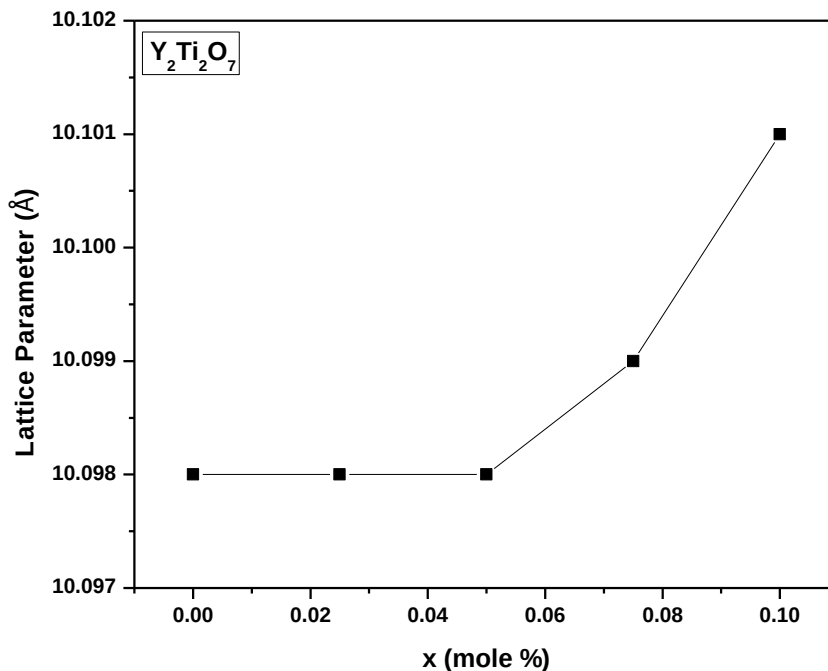


Figure 4.9: The lattice parameter as a function of Sr concentration (x) in $Y_{1-x}Sr_xTiO_y$.

The lattice parameter calculated for YST ($x=0$) and YST-1 ($x=0.1$) sample shows slight increase e.g., 10.09 Å for YST and 10.10 Å for YST-1. In general, higher ionic radii doping increases the lattice parameter which is in agreement with our observed data. It might be possible that in YST sample, titanium might be present in the mixed state Ti^{3+}/Ti^{4+} whereas in YST-1 sample this ratio decreases which may lead to lower the lattice parameter slightly. The mixed state of titanium in $Y_2Ti_2O_7$ is well reported in literature [24]. The presence of mixed state of titanium can also be correlated with the data of TG/DTA of YST and YST-1 samples performed in air and discussed in later part of the thesis. In other words, the doping of Sr^{2+} not only increases the density but also ordering in the present system e.g., YST-2. Moreover, there is no extra XRD peak (except a small kink at lower angle) with no apparent change in lattice parameter, so solubility limit of Sr^{2+} in $Y_2Ti_2O_7$ is $x \geq 0.050$. A similar case of Al^{3+} solubility was reported in

$\text{Gd}_2(\text{Ti}_{1-y}\text{Al}_y)_2\text{O}_7$ system by Kramer et al., [1]. Moreover, the lattice parameter in the present system is slightly smaller than other reported pyrochlores [25, 26].

4.1.3 FT-IR analysis

FT-IR spectrum is a well-known approach to demonstrate the cubic pyrochlore structure. There are seven characteristic absorption bands in the region $100\text{--}1200\text{ cm}^{-1}$ for the pyrochlore compounds with the formula of $\text{A}_2\text{B}_2\text{O}_7$ [27]. FT-IR spectra of YT-1 and YT-2 samples are shown in figure 4.10.

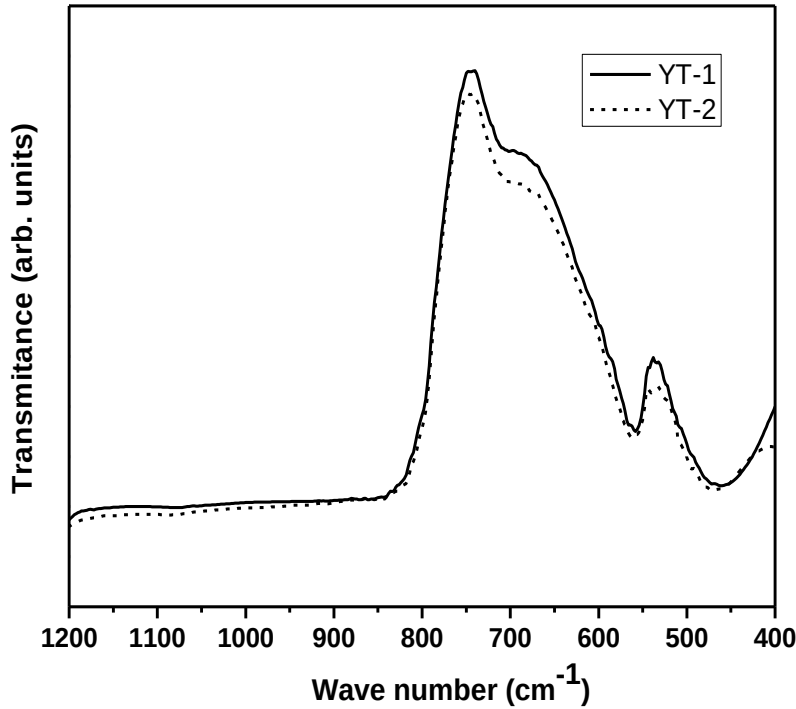


Figure 4.10: FT-IR spectra of YT-1 and YT-2 samples.

The figure depicts that the samples exhibit similar FT-IR spectra except more diffused bands in YT-2 sample as compared to YT-1 sample. It is manifestation of higher disorder in YT-2 sample. In FT-IR spectra the bands are formed by bending and stretching vibrations of metal oxygen bonds in pyrochlore [28]. The band in $600\text{--}700\text{ cm}^{-1}$ region corresponds to B-O stretching

vibration in BO_6 octahedron. The band at 500 and 400 cm^{-1} can be attributed to A-O' and A-O stretching vibration in the $\text{AO}_6\text{O}_2'$ polyhedron of $\text{A}_2\text{B}_2\text{O}_7$ [28]. An FT-IR spectrum of YT-2 and YT-1 clearly exhibits four transmission bands with slight variation in intensity and position. The absorption bands are observed at nearly 460 which is due to A-O' (A = Y) stretching vibration. Similarly, two absorption bands are identified at 580 and 700-680 followed by broad weak absorption at 820 which can be assigned to Ti-O stretching vibration in TiO_6 octahedron in pyrochlore system [17].

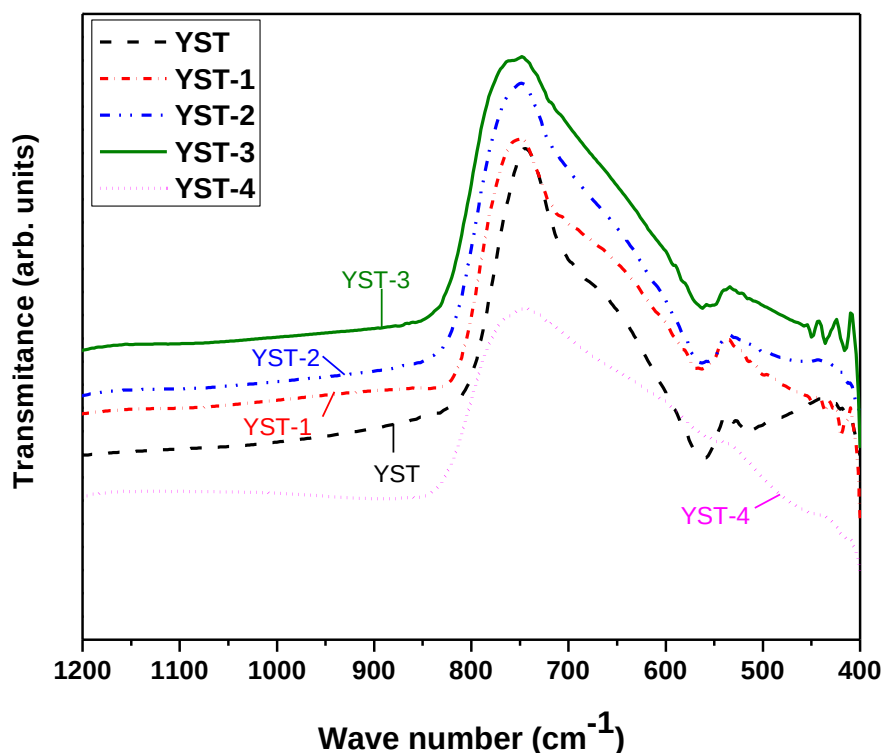


Figure 4.11: FT-IR spectra of YST, YST-1, YST-2, YST-3 and YST-4 samples.

FT-IR spectra of YST, YST-1, YST-2, YST-3 and YST-4 samples are shown in figure 4.11. All the samples exhibit similar FT-IR spectra as observed for YT-1 and YT-2 samples except some change in band intensity. FT-IR spectrum of YST, YST-1, YST-2, YST-3 and YST-4 samples

clearly exhibit Ti-O and Y-O stretching vibration bands with slight variation in intensity and position. The absorption bands are observed at nearly 440 for YST, 410, 432, 440 for YST-1, 440 for YST-2, 410, 426, 443, 456 for YST-3 and 440 for YST-4 respectively which is due to A-O' (A=Y) stretching vibrations. These bands are sharp and fully resolved in YST-1 and YST-3 samples as compared to YST, YST-2 and YST-4 samples which show higher ordering in YST-1 and YST-3 samples. This hypothesis is also supported by the XRD results of these samples. Similarly, two absorption bands are identified at 540 and 680 for YST, 536 and 670 for YST-1, 540 and 660 for YST-2, 538 and 650 for YST-3 and 535 and 600 for YST-4. Above bands are followed by broad weak absorption bands at 810-840 for all the samples which can be assigned to Ti-O stretching vibration in TiO_6 octahedron in pyrochlore system [16]. Broadening in 440 band, after doping of Sr^{2+} , particularly in YST-2 and YST-4 samples is a clear manifestation of weakening of A-O' bond (A=Y) [29]. It may be associated with formation of mixed bond of Y-O and Sr-O in these samples. It is observed that among all the samples, the FT-IR spectra of YST-4 exhibit higher broadening in all the bands which are a clear indication of weakening of pyrochlore phase as also observed in XRD. The Sr^{2+} addition leads to weakening of the host matrix in YST-2 sample to YST-4 samples.

On the other hand, FT-IR spectrum of YCT-1, YCT-2, YCT-3 and YCT-4 samples clearly exhibit similar bands as observed for YT-1, YT-2 and Sr doped samples. The absorption bands are observed at nearly 440 for YCT-1, 460 for YCT-2, 460 for YCT-3 and 440, 460 for YCT-4, respectively which is due to A-O' (A = Y) stretching vibrations. These bands are sharp and fully resolved in YCT-4 sample as compared to YCT-1, YCT-2 and YCT-3 samples which show higher ordering in YCT-4 sample as shown in figure 4.12.

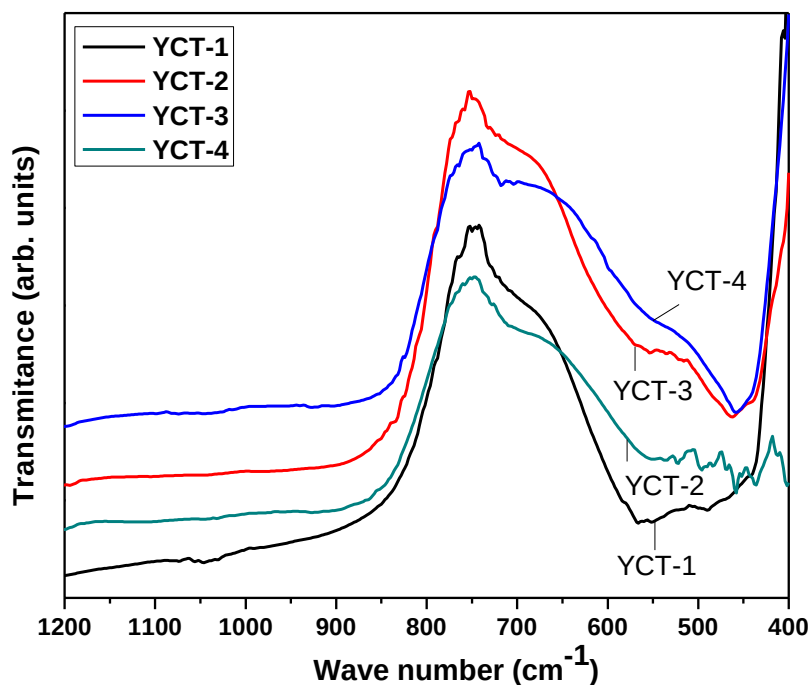


Figure 4.12: FT-IR spectra of YCT-1, YCT-2, YCT-3 and YCT-4 samples.

Similarly, two absorption bands are identified at 570 and 720 for YCT-1, 550 and 720 for YCT-2, 550 and 720 for YCT-3, 500, 520, 720 for YCT-4. Above bands are followed by broad weak absorption bands at 810-840 for all the samples which can be assigned to Ti-O stretching vibration in TiO_6 octahedron in pyrochlore system [17]. Whereas, Ca-O peak appears at 300cm^{-1} - 400cm^{-1} is not observed in the figure 4.12 [30]. In addition to this, FT-IR spectra shows sharp absorption band around 1100 cm^{-1} in YCT-1 sample which disappears in other samples indicating the presence of Ti-O band. The appearance of absorption bands around 1750 cm^{-1} in YCT-3, YCT-4 samples and around 2400 cm^{-1} in all the samples can be attributed to the presence of Ca-O band. In other words, as the concentration of calcium increases in the samples from $x = 0.1$ to $x = 0.4$, the absorption band becomes more prominent in YCT-4 sample as

compared to other samples. Moreover, peaks of lesser intensity around 1450 cm^{-1} , 3600 cm^{-1} , 1650 cm^{-1} and 3700 cm^{-1} which are due to CaO and TiO_2 powder are observed [31]. Conclusively, FT-IR spectra of all the samples show the presence of Ti-O and Y-O bands due to $\text{Y}_2\text{Ti}_2\text{O}_7$ phase. The host matrix of pyrochlore becomes weak with addition of Sr^{2+} and Ca^{2+} in doped samples as compared to YT-1 and YT-2 samples.

4.1.4 SEM and EDS analysis

The gold plated fractured surface of Y-1 and Y-2 was analyzed under SEM. The micrograph indicates the presence of single phase fine grain structure (figure 4.13 (a)). The grain size is observed to be non-faceted with nearly uniform size (6 to $10\text{ }\mu\text{m}$). The structure is homogeneous throughout the section (figure 4.13 (b)). However, porosity can also be visualized at some places. The overall analysis presents uniform single phase structure of the Y-2 sample having uniform grain size. The SEM micrographs of fractured surfaces of Y-1 sample are shown in figure 4.14 (a-d). It is observed that the sintered Y-1 sample has a fine-grained microstructure with faceted morphology as shown in figure (4.14(a)) in which typical structure is observed for YTiO_3 . The grain size varies from $23\text{ }\mu\text{m}$ to $64\text{ }\mu\text{m}$ with irregular porosity. The grain size observed for Y-1 sample (YTiO_3 phase) is bigger than Y-2 sample ($\text{Y}_2\text{Ti}_2\text{O}_7$ phase). As sintering proceeds partial melting occurs. This causes formation of solid solution phase. During fast heating the impurities (whatever may be) forms a thin low melting point glassy substance. This encapsulates the entire structure, thus stopping the diffusion of oxygen. The presence of traces of chloride (as TiO_2 and Y_2O_3 are made by oxidation of TiCl_4 and YCl_3) ion inside the material produces reducing atmosphere.

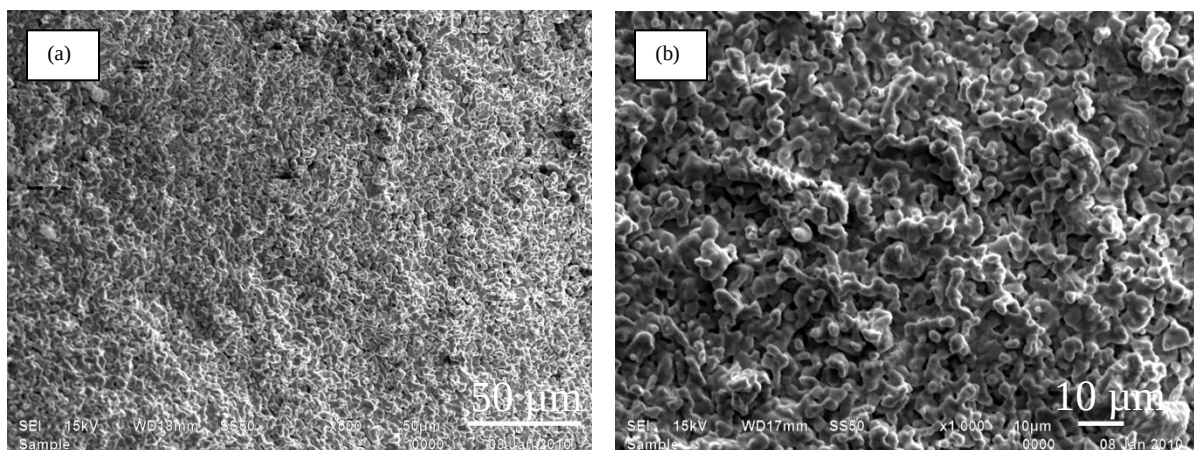


Figure 4.13: SEM micrographs of Y-2 sample at various magnifications.

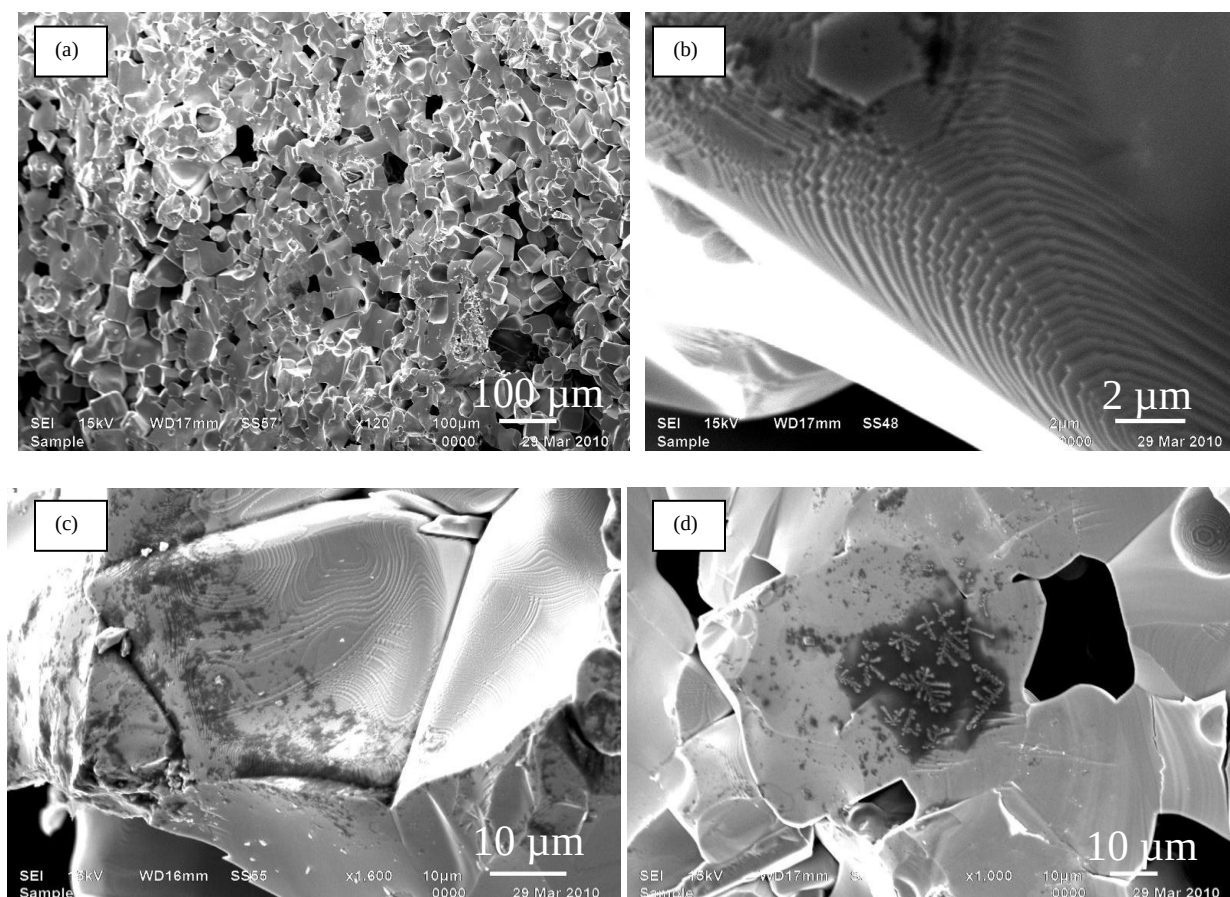


Figure 4.14: SEM micrographs of Y-1 sample at various magnifications.

The structural features indicate that growth of YTiO_3 occurs by melting process. The encapsulated layer provides sufficient amount of under cooling of the melt. The faceted growth

morphology of this phase occurs in steps which can be seen more clearly in figure 4.14 (b). The faceting behavior of interface was analyzed by Jackson by introducing the concept of roughness parameter (α) which depends on entropy of solution [32]. Later on, Saroch et al., [33] proposed a thermodynamic model to explain the faceting behavior of primary phase which emphasizes the importance of composition and temperature dependence of entropy of solution ($d\Delta S^{al}/dT$) of primary phase. The role of $d\Delta S^{al}/dT$ in controlling faceting behavior can be understood in conjunction with the under cooling introduced by growth rate. Since the thin glassy phase observed at the surface of melt exists, it provides sufficient amount of under cooling, causing a higher growth rate. Because of this the equilibrium at the solid-liquid interface tends to shift to that characteristic of under cooled temperature. This causes an increase in ΔS^{al} parameter which may lead to exhibit faceting morphology as per Jackson's model [32] which has been successfully demonstrated also for other systems [34, 35]. The flow pattern observed from the torched area indicates that some low melting point liquid phase has formed which provides reducing atmosphere (figure 4.14 (c)). The black spots observed within the grain also support this evidence as this seems to be rich on metal side. The dendrites observed within these grains are rich in Ti indicating that this is of metal Ti. The EDS analysis done on entire surface at low magnification indicate that the substance is deficient in oxygen content which is very close to $YTiO_3$ (figure 4.15 (a) and table 4.3).

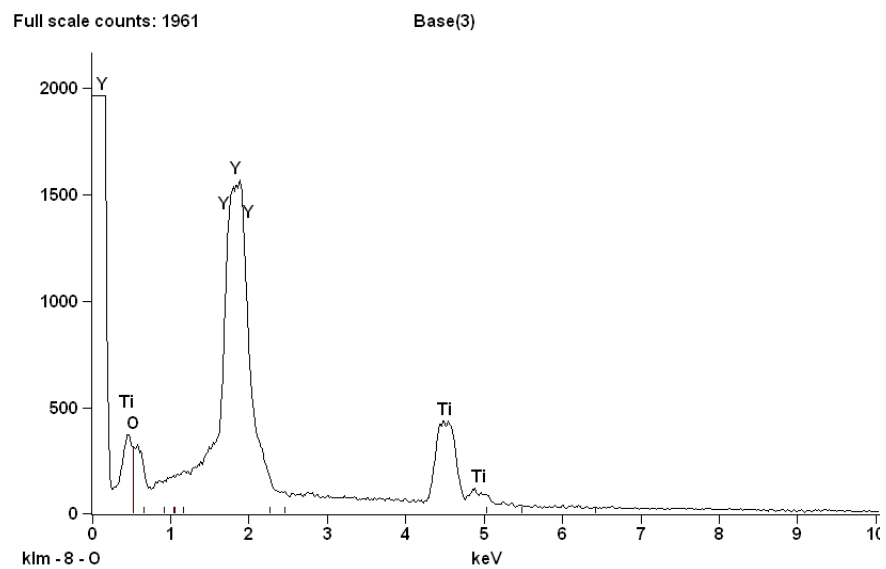


Figure 4.15(a): EDS spectrum of Y-1 sample.

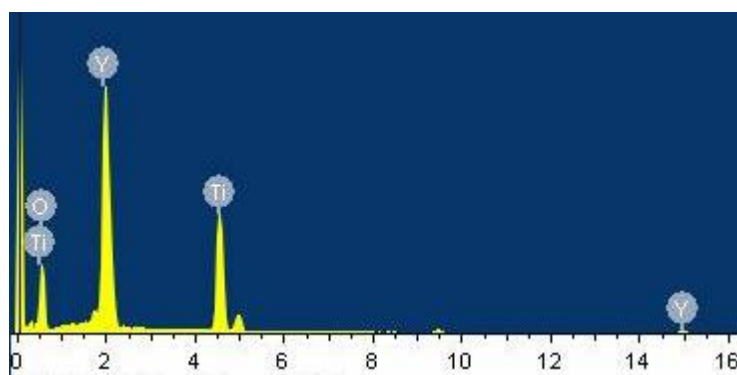
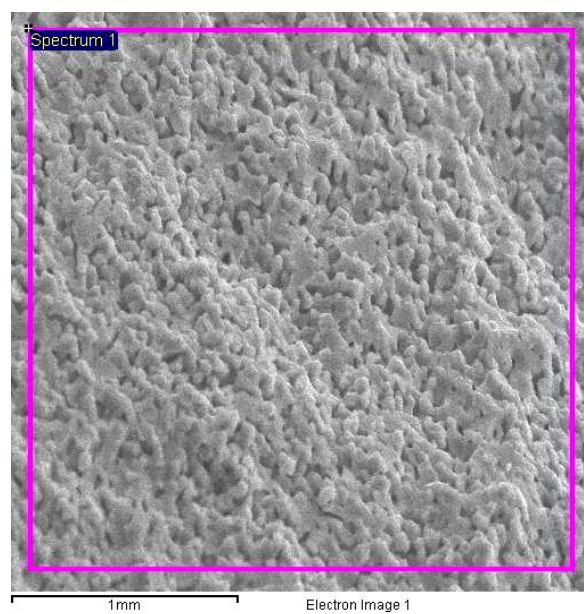


Figure 4.15(b): EDS spectrum of Y-2 sample.

Table 4.3: Results of EDS analysis of Y, Ti and O in the Y-1 sample and Y-2 sample as indicated in figure 4.15 (a) and figure 4.15 (b), respectively.

Sample Name	Y-1		Y-2	
Element Line	Weight (%)	Atom (%)	Weight (%)	Atom (%)
O K	53.43	81.56	40.31	74.53
Ti K	24.04	12.26	19.70	12.16
Y L	22.53	6.19	40.00	13.31
Total	100.00	100.00	100.00	100.00

Whereas, the EDS analysis done on surface of Y-2 sample indicate that the measured atomic percentage agrees with the compound stoichiometry. The EDS done on the dendrite indicate that it is rich in Ti so the dendrite growth of Ti has occurred (figure 4.16 and table 4.4).

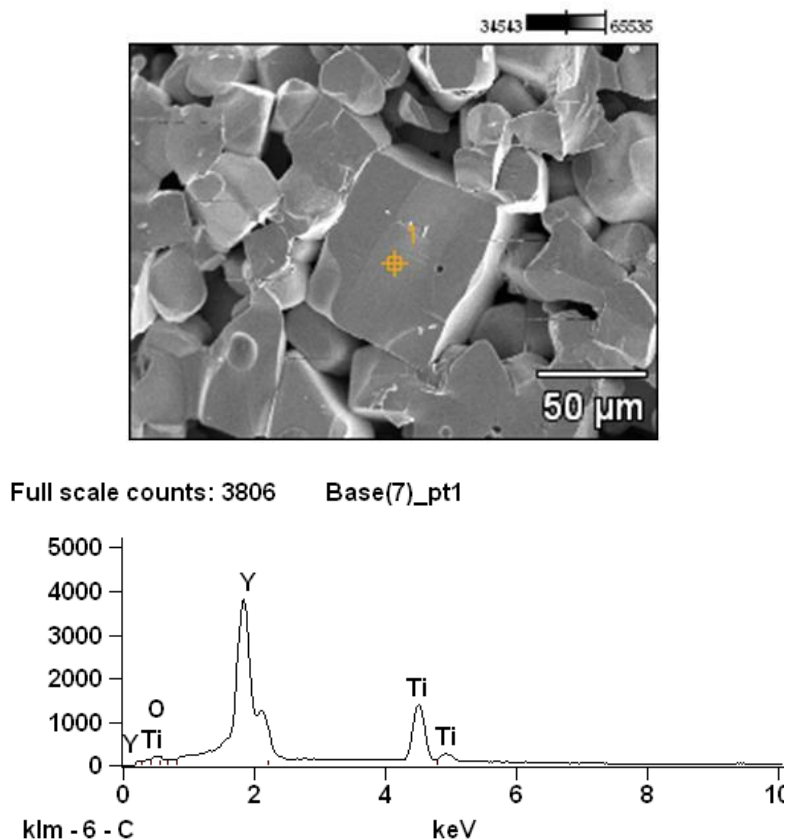


Figure 4.16: SEM images and the EDS spectrum of Y-1 sample.

Table 4.4: Spot analysis of individual grain showing presence of Y, Ti and O in the Y-1 sample as indicated in figure 4.16.

Elements	Weight (%)	Atom %
Y-L	22.65	10.35
Ti-K	63.12	53.51
O-K	14.24	36.14

On the other hand, the SEM micrographs of fractured surfaces of YST ($x=0$), YST-1 ($x=0.1$), YST-2 ($x=0.2$), YST-3 ($x=0.3$) and YST-4 ($x=0.4$) samples are shown in figure 4.17 respectively. Moreover, it is clearly observed that grain size of all the sample varies between 3 to 11 μm with irregular porosity as shown in table 4.5.

Table 4.5: Averaged grain size of YST, YST-1, YST- 2, YST-3 and YST-4 samples.

Sample Name	YST	YST-1	YST-2	YST-3	YST-4
Grain Size (μm)	3	11	5.5	5.0	4

The distributions of the grains are non-uniform in all the samples. The YST sample is porous and pores are continual as well as open. On the other hand, YST-1 sample includes grains with closed pores. YST-1 sample reaches intermediate stages of sintering where shrinking of pores occur by reduction in their cross-section. Due to this, density of YST-1 sample increases slightly as depicted in table 4.1. In contrast to this, YST-2 sample is dense with pores trapping within the grains. However, in YST-3 sample with Sr ($x = 0.3$) results in the formation of continual crack in the sample due to which conductivity decreases suddenly by two orders as mentioned in table 4.9 (discussed later). In YST-4 sample, higher addition of Sr on Y-site results in significant grain growth with decrease in porosity having isolated pores.

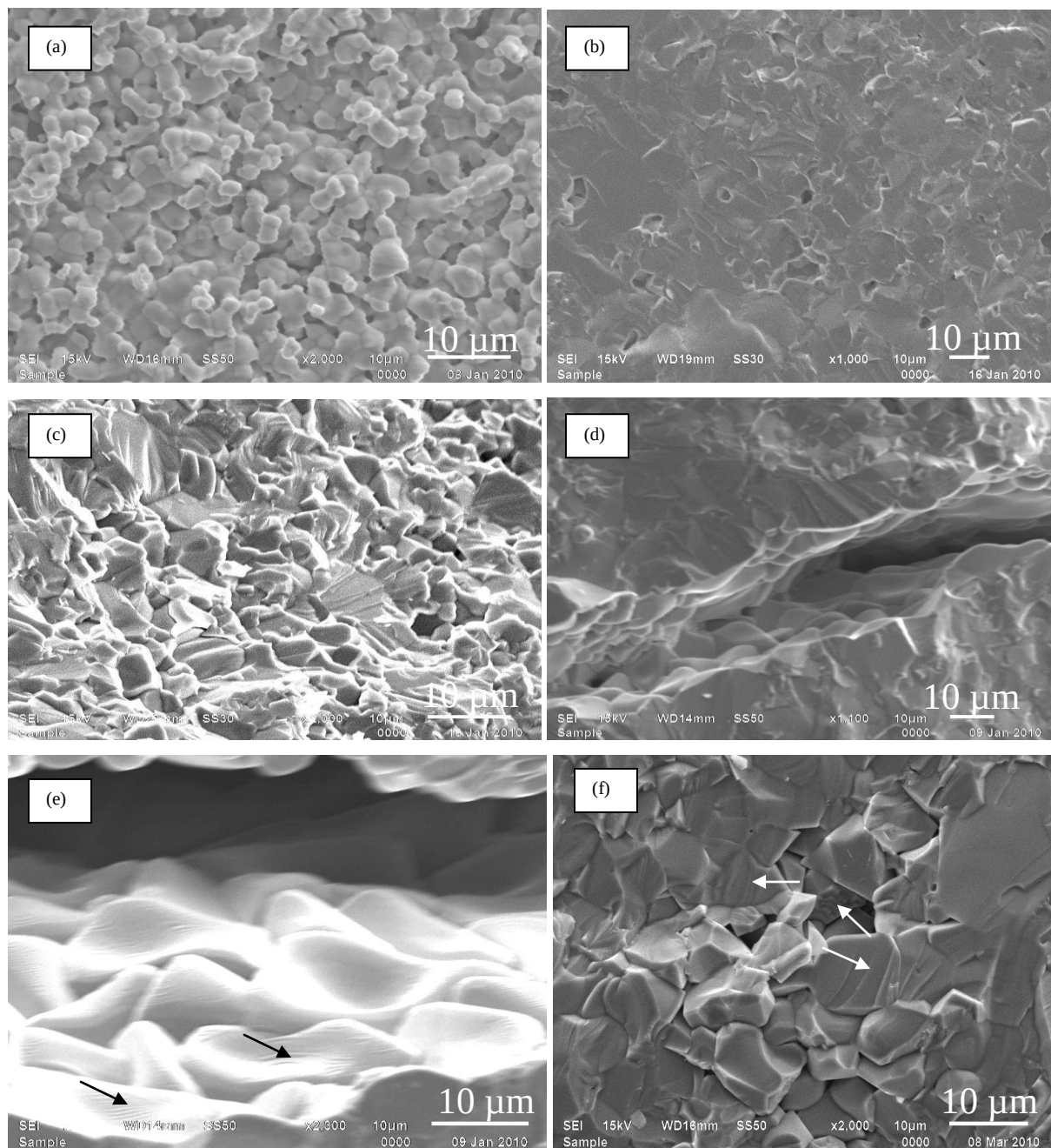


Figure 4.17: SEM micrographs of fractured surfaces of (a) YST ($x=0$), (b) YST-1 ($x=0.1$), (c) YST-2 ($x=0.2$), (d) YST-3 ($x=0.3$), (e) YST-3 ($x=0.3$) (inside crack) and (f) YST-4 ($x=0.4$), respectively.

The SEM micrograph of YST-4 sample suggests that grains are very close. The grain growth decreases with increase in Sr-doping from $x=0.1$ up to $x=0.3$. The grain growth in SrTiO_3 has been reported to be highly sensitive to O_2 acceptor-doping [5-7]. Thus, with increase of SrTiO_3 phase along with $\text{Y}_2\text{Ti}_2\text{O}_7$ as shown in XRD in YST-2, YST-3 and YST-4 samples, impedes the mass transportation and the sintering process leading to continuous crack in YST-3 sample and decrease in density of YST-4 sample [23]. The critical features observed in all these micrographs are that morphology of YST sample is different from doped one (YST-1 to YST-4). The sintered sample (YST) analyzed in fractured mode exhibit round shape agglomerated particles with small porosity. However, in case of YST-1 sample the surface topography of fractured surface has changed from round to faceted type. Though this variation is not much but observable. This has happened because of nucleation of SrTiO_3 phase. These structural features get resolved for YST-2 to YST-4 samples. The presence of river flow pattern inside the grain differentiates it from the undoped YST sample. These structural features grow in a defined direction with faceted morphology. In case of YST-3 sample apart from faceted features a long continual crack is also observed which was not present at the surface of pellet. The cracks might have developed due to internal stresses. These internal stresses have built up during sintering of the sample. However, when conductivity measurement was done it has lead to formation of crack even for other samples of same composition. Because of presence of this crack the conductivity was observed to fall drastically. This crack has appeared inside the sample when the lattice is in strained condition. When analyzed critically, one can see the fully grown faceted structure along the periphery of crack on bottom side of the micrograph. However, the upper side structure exhibit very fine ladder type of morphology which is arising due to internal stress. However, when analyzed inside the crack the features appear to be relaxed one. Each grain grows with the shapes

like lake and within the grain one could see the growth of fine lamellar type of structure. This shows that SrTiO_3 phase is nucleating from the matrix of single phase SrO doped $\text{Y}_2\text{Ti}_2\text{O}_7$. As the crystal attains the super saturation it rejects extra Sr as SrTiO_3 which grows in parallel fashion. With increase in SrO concentration this fine needles like SrTiO_3 thickens and form banded structure as can be seen in YST-4 sample (marked arrow). The higher ionic conductivity observed for YST-4 sample is only due to growth of this phase (SrTiO_3). In addition to this, the SEM micrographs of fractured surfaces of Ca doped samples i.e., YCT-1 ($x = 0.1$), YCT-2 ($x = 0.2$), YCT-3 ($x = 0.3$) and YCT-4 ($x = 0.4$) are shown in figure 4.18 respectively. It is clearly observed from the SEM micrographs that grain of all the samples are of different sizes with irregular porosity. The distribution of the grains is irregular and non uniform in all the samples. The YCT-1 sample consists of grains with closed pores and river flow pattern is observed on certain grains. In contrast, YCT-2 and YCT-3 samples consist of pores which are open and continuous resulting in decrease in densities of these samples in comparison with YCT-1 sample. On the other hand, YCT-4 sample indicates the formation of small cracks between adjoining grains due to which conductivity decreases suddenly by two orders as mentioned in table 4.9 (discussed later).

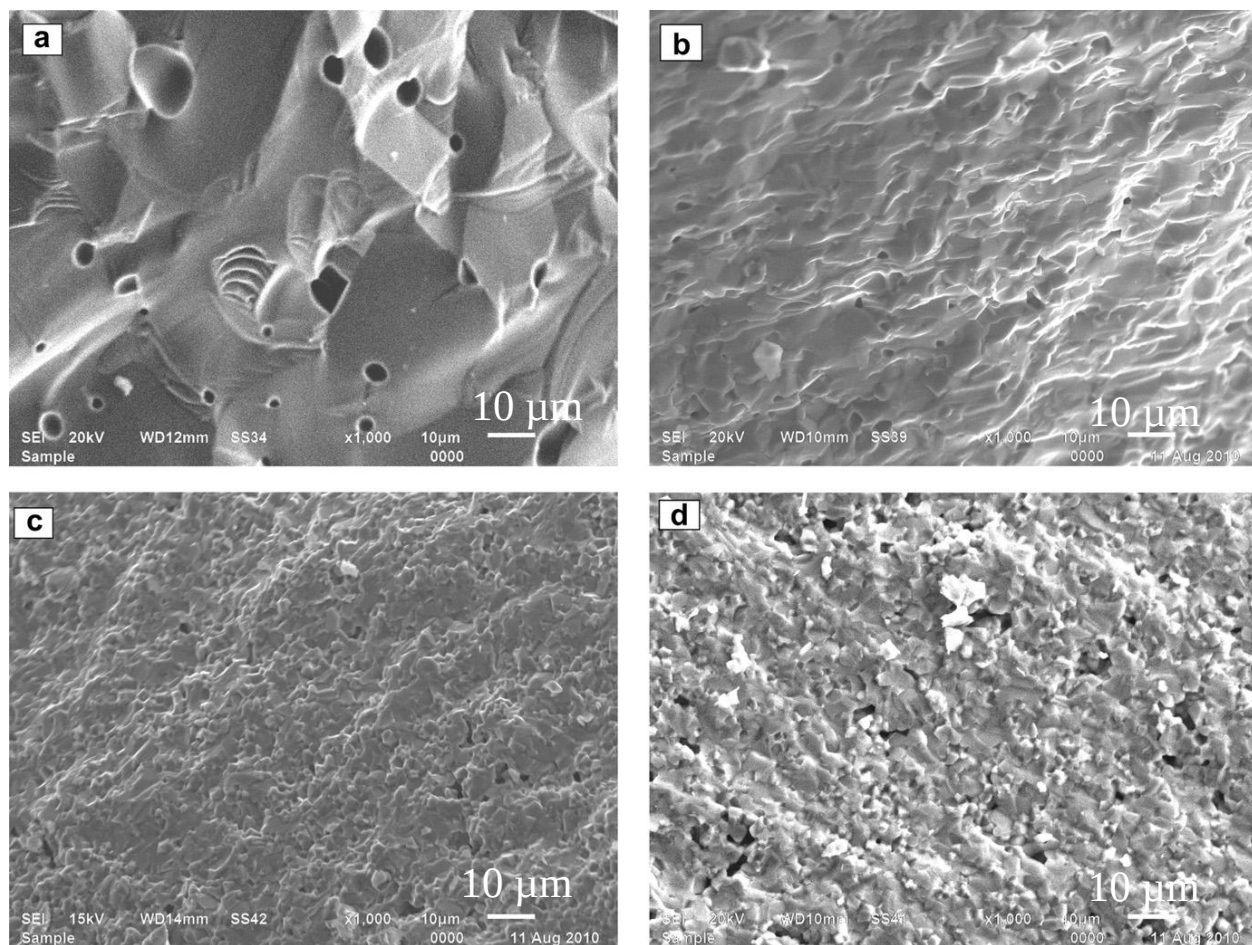


Figure 4.18: SEM micrographs of fractured surfaces of (a) YCT-1, (b) YCT-2, (c) YCT-3 and (d) YCT-4, respectively.

In YCT-4 sample, higher addition of Ca on A-site results in increase in porosity and decrease in density. In other words, with increase of CaTiO_3 phase along with $\text{Y}_2\text{Ti}_2\text{O}_7$ as shown in XRD for YCT-2, YCT-3 and YCT-4 samples a decrease in density is observed. The critical features observed in all these micrographs are that morphology of YCT-4 sample is different from (YCT-1 to YCT-3). The sintered samples (YCT-1 to YCT-3) when analyzed in fractured mode exhibit faceted shape grains with small porosity. However, in case of YCT-4 sample the surface topography of fractured surface clearly indicates the presence of two phases i.e. $\text{Y}_2\text{Ti}_2\text{O}_7$ and CaTiO_3 . Though this variation is not very pronounced but observable. This has happened

because of nucleation of CaTiO_3 phase. These structural features get resolved for YCT-1 to YCT-3 samples. Whereas, presence of river flow pattern inside the grain is observable in all the samples. These structural features grow in a defined direction with faceted morphology. The EDS analysis done on surface of YCT-1 sample indicates clearly the presence of $\text{Y}_2\text{Ti}_2\text{O}_7$ phase (figure 4.19(a) and table 4.6). The point analysis done on YCT-4 sample indicates that sample is rich in CaTiO_3 phase along with the presence of $\text{Y}_2\text{Ti}_2\text{O}_7$ phase (figure 4.19(b) and table 4.7). The overall analysis indicates that volume fraction of CaTiO_3 phase increases with increase in calcium content in YCT series. The EDS analysis indicates that the measured atomic percentage is in agreement with the compound stoichiometry. SEM analysis of YCT series samples clearly show that the presence of secondary phase ATiO_3 ($A = \text{Sr, Ca}$) works as grain growth inhibitor and it is very prominent in case of Ca doped samples for some cases. Whereas, the secondary phase also lead to formation of cracks in the samples.

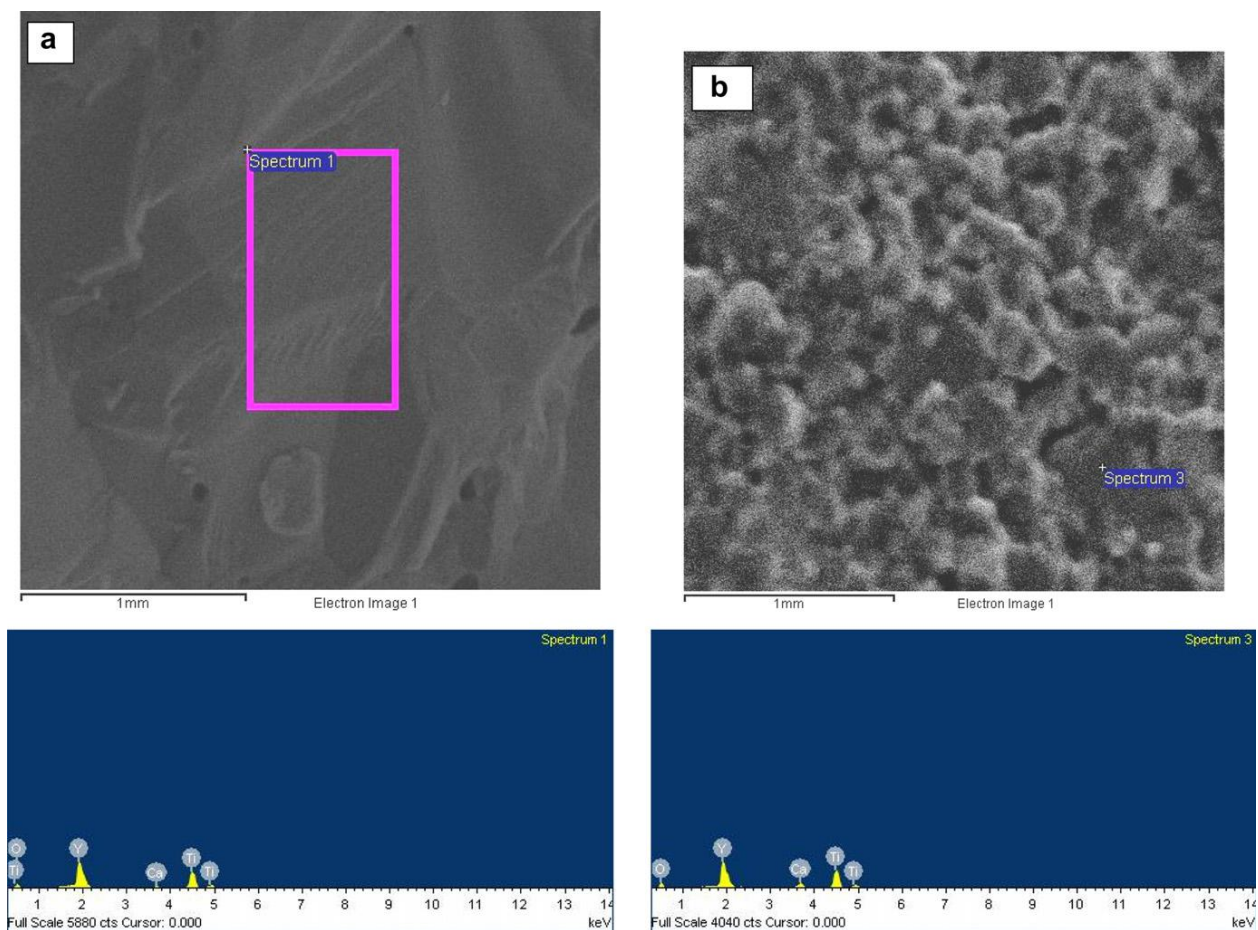


Figure 4.19: EDS analysis of fractured surfaces of (a) YCT-1 and (b) YCT-4, respectively.

Table 4.6: EDS analysis done on surface of YCT-1 sample.

Element	Weight (%)	Atomic (%)
O	30.34	64.14
Ca	1.38	1.17
Ti	26.76	18.90
Y	41.52	15.80

Table 4.7: EDS analysis done on surface of YCT-4 sample.

Element	Weight (%)	Atomic (%)
O	34.73	67.78
Ca	4.18	3.25
Ti	24.98	16.28
Y	36.11	12.68

4.1.5 Thermal analysis

Thermo gravimetric analysis of samples YT-1 and YT-2 are shown in figure 4.20. Both the graphs indicate weight loss below 200 °C temperature. It might have incurred because of release of adsorbed water [37]. Second plateau in the both samples corresponding with $T_{\max} = 340$ °C can be designated on the basis that some rearrangement in the internal structure has taken place. Sharp weight gain is exhibited by YT-2 sample at 550 °C. This sharp change could be attributed due to transition of order to disordered pyrochlore. These transitions are contributed due to variation in composition, temperature and pressure [37].

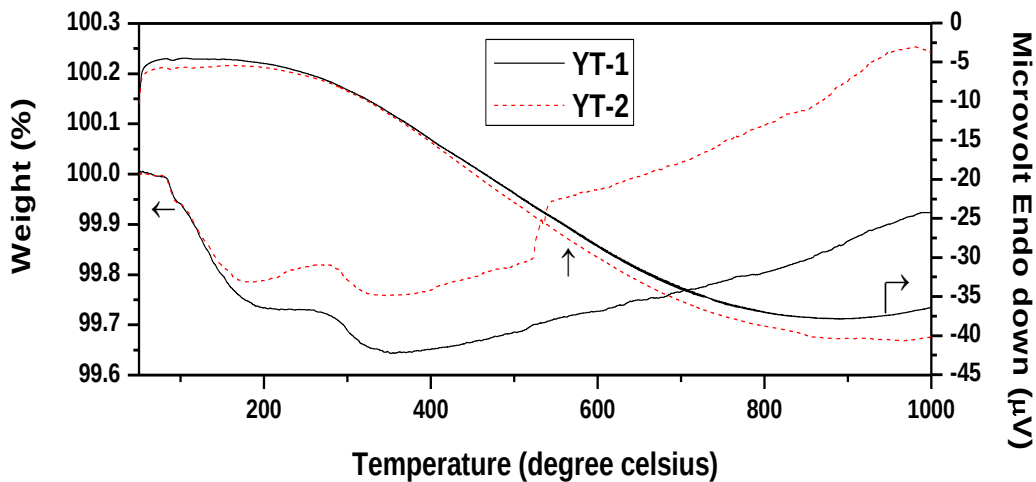
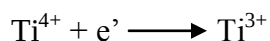


Figure 4.20: TGA and DTA analysis of YT-1 and YT-2 samples.

Moreover, a deviation in DTA plots have been observed at nearly 540 °C as shown by the arrow marked (figure 4.20). After that YT-2 sample shows increasing weight gain up to 950 °C which is due to absorption of oxygen atoms from the air since TGA was performed in air [38]. The sintering temperature of YT-2 sample (1550 °C) is greater than YT-1 sample (1500 °C). At higher temperature oxygen partial pressure reduces which is in the case for YT-2 sample. Due to this, higher disordering occurs in YT-2 sample as compared to YT-1 sample. The conductivity

data of YT-2 sample also shows the fluctuations at 550 °C (figure 4.26) (discussed later). On the other hand, YT-1 sample shows no such appreciable change. It clearly indicates that YT-2 sample exhibits higher oxygen vacancies due to transformation of Ti^{4+} to Ti^{3+} . The Kroger-Vink notation for this transformation is



In other words, a slight amount of oxygen loss may occur. TGA of Y-1 and Y-2 samples are performed in two different atmospheres as shown in the figure 4.21 (a) and (b). The weight change in nitrogen and air atmospheres are 0.29% and 0.85% in Y-1 sample and 0.48% and 0.41% in Y-2 sample, respectively. Figure 4.21 (a) indicates weight loss below 200°C in Y-1 sample when TGA was taken in nitrogen atmosphere. It might have incurred because of release of adsorbed water [36]. Second plateau in TGA curve of sample Y-1 (figure 4.21 (a)) is observed corresponding to 340°C. It might be related to strain relaxation in the samples [13]. Moreover, the peak shifting towards lower angles observed in XRD clearly indicates that the Y-1 sample is in highly strained condition.

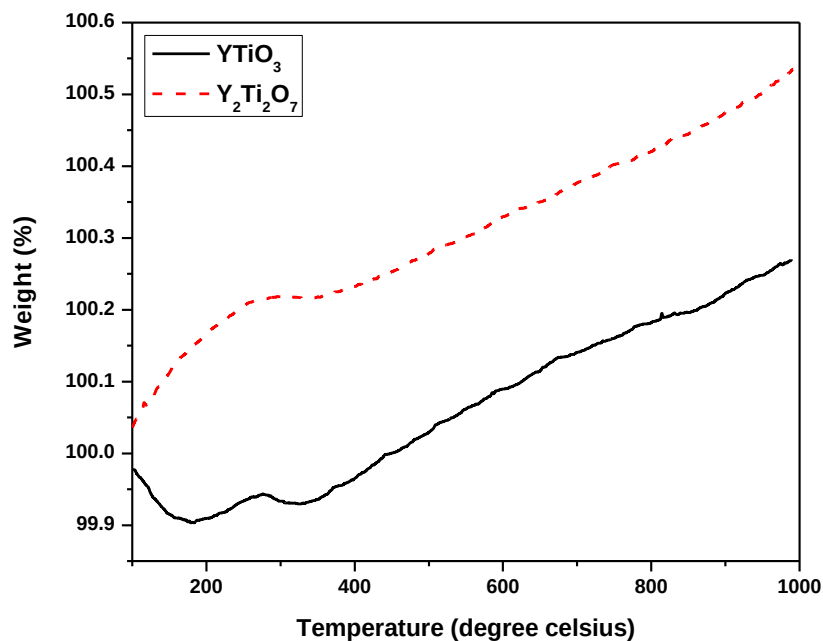


Figure 4.21 (a): Thermo gravimetric analysis of Y-1 and Y-2 samples in nitrogen atmosphere.

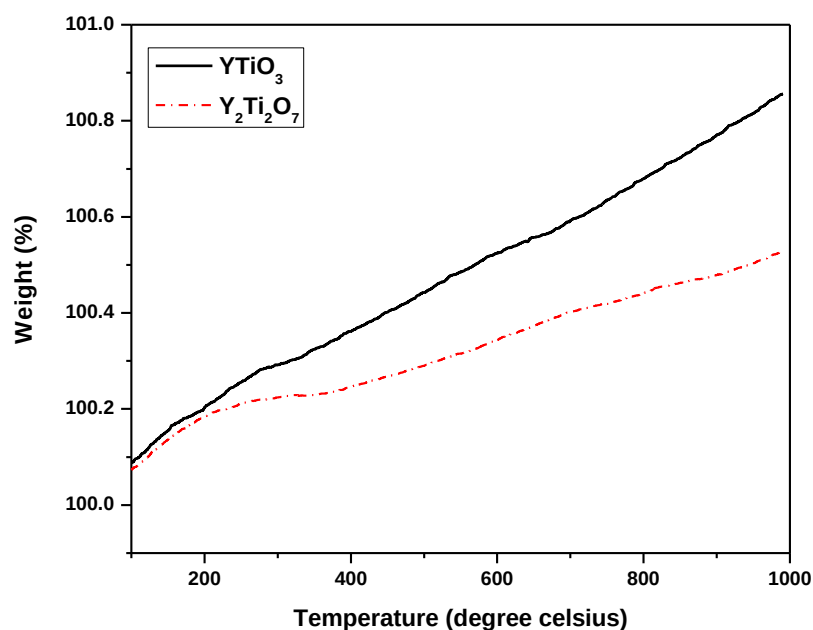


Figure 4.21 (b): Thermo gravimetric analysis of Y-1 and Y-2 samples in air.

Compared to this an opposite phenomenon is observed when thermal analysis of this sample was done in air (figure 4.21 (b)). Here the weight gain is observed. During heating the loss in weight occurs due to release of adsorbed water. However, in oxidizing atmosphere the decomposition of YTiO_3 occurs [39]. Since the later stage mechanism is dominating, so net weight gain occurs. Conclusively, it can be interpreted from these results that two different mechanism (water loss) and decomposition of YTiO_3 (weight gain) are operative in this temperature region which ultimately leads to little weight gain when sample is exposed in air. There are ample reports regarding decomposition of YTiO_3 in air atmosphere due to oxidation of Ti^{3+} to Ti^{4+} [39]. On the other hand, slight kink observed in Y-2 sample between 350°C and 400°C can also be designated due to tensile strain relaxation which is opposite to the relaxation observed in Y-1 sample. In addition to this, pyrochlore sample Y-2 shows the weight gain throughout the tested temperature range ($500\text{-}1000^\circ\text{C}$). This change in weight % is approximately similar when performed under two different atmospheres (air and nitrogen). Similar behavior observed for Y-2 sample is manifestation of higher stability with lower content of oxygen vacancies as compared to Y-1 sample. The weight gain at higher temperature in both curves in samples Y-1 and Y-2 might also be attributed due to some rearrangement in the internal structure in presence of two different atmospheres. On the other hand, in higher temperature region, Y-1 sample (in air atmosphere) exhibits higher weight gain than in nitrogen atmosphere. It also indicates the presence of higher oxygen vacancies in the Y-1 sample as compared to Y-2 sample where weight gain is less than Y-1 sample. During experiment, the oxygen might occupy the vacant sites in the sample and charge compensation takes place by transformation of Ti^{3+} to Ti^{4+} state. Moreover, in Y-1 sample, instability of Ti^{3+} to Ti^{4+} transition leads to an excess of oxygen above the exact stoichiometry formula and oxidation take place above 450°C in air atmosphere [40]. However, in

literature weight loss with increase in temperature is found to exhibit by Mn doped $\text{Y}_2\text{Zr}_2\text{O}_7$ and undoped $\text{Y}_2\text{Zr}_2\text{O}_7$ systems [41]. According to them, weight loss results from the loss of lattice oxygen as the materials become oxygen deficient with increasing temperature. Escudero et al., [42] investigated $\text{La}_4\text{Sr}_8\text{Ti}_{11}\text{Mn}_{1-x}\text{Ga}_x\text{O}_{38-\delta}$ ($x = 0, 0.25, 0.50, 0.75$ and 1.0) system by TGA measurement. They have reported weight gain which can be attributed due to oxygen vacancies. Similar to Y-1 and Y-2 samples, thermal gravimetric analysis of Sr doped samples i.e., YST, YST-1, YST-2, YST-3 and YST-4 samples done in nitrogen atmosphere is shown in figure 4.22 and figure 4.23 which also depicts TGA as well as DTA done in air atmosphere.

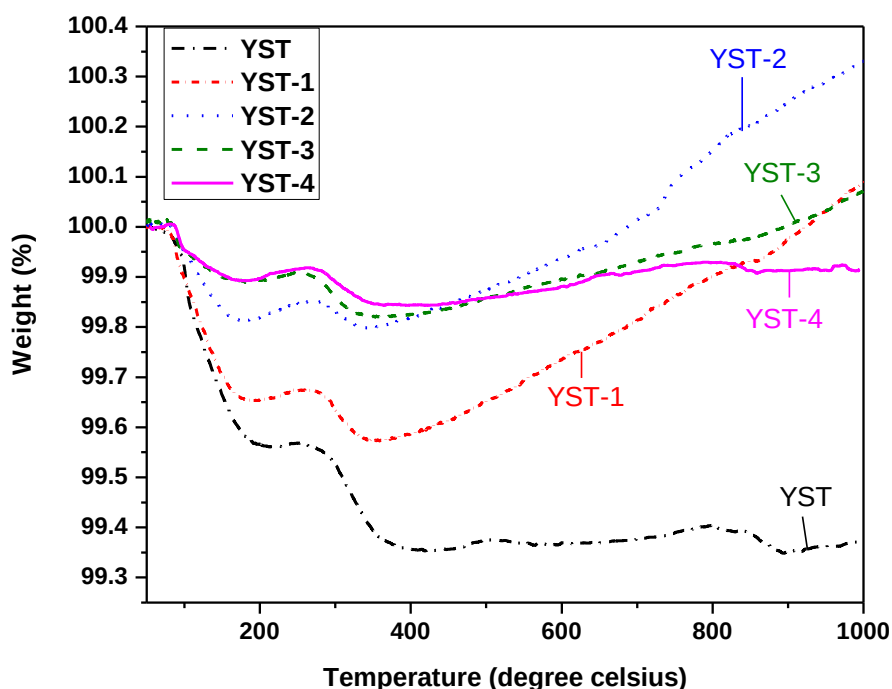


Figure 4.22: Thermo gravimetric analysis of YST, YST-1, YST-2, YST-3 and YST-4 samples in nitrogen atmosphere.

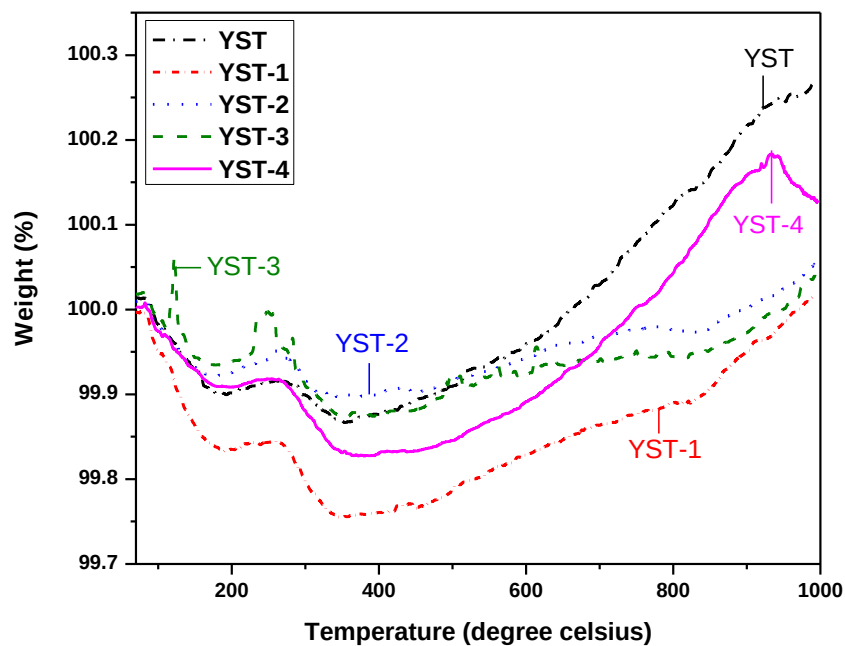


Figure 4.23 (a): Thermo gravimetric analysis of YST, YST-1, YST-2, YST-3 and YST-4 samples in air atmosphere.

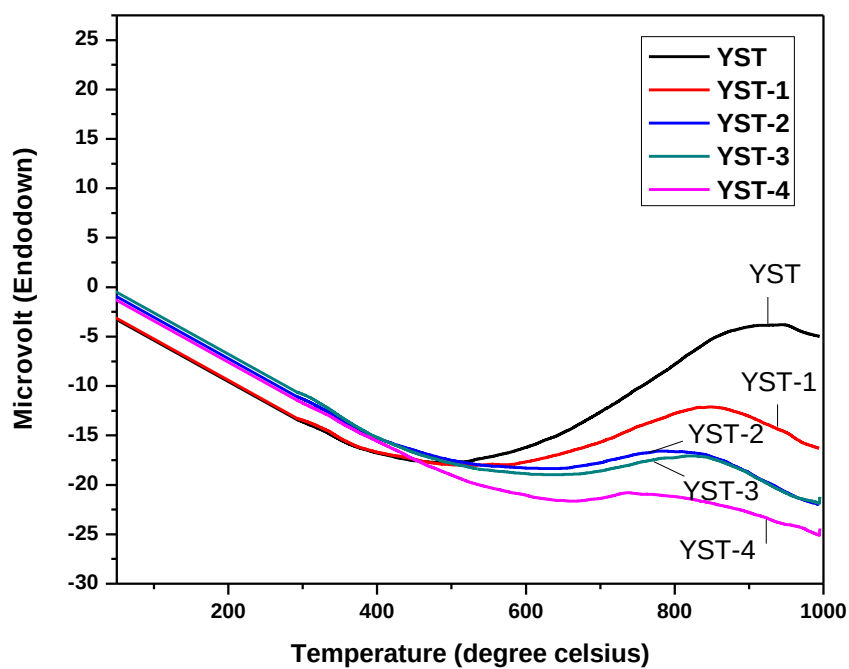


Figure 4.23 (b): Differential thermal analysis of YST, YST-1, YST-2, YST-3 and YST-4 samples in air atmosphere.

All the graphs show weight loss below 200°C temperature. Second peak observed in TGA of all the samples in between 350°C and 400°C can be designated for some strain relaxation. The weight gain at these temperatures (300-400°C) is also associated with oxidation of Ti^{3+} [24]. Similar behavior of weight gain is also obtained in YST and YST-1 samples at low temperature showing that oxidation states of titanium exist as a mixture of $\text{Ti}^{3+/4+}$. Strikingly, undoped sample in nitrogen atmosphere could not show any appreciable change after 380°C, showing its high stability with increase of temperature whereas weight gain is exhibited by the sample after 500°C when performed in air atmosphere. This can be due to the presence of oxygen vacancies in the sample. Nasraoui et al, [36] has reported good stability for different pyrochlore systems. This is in consistent with reported TG of $\text{Yb}_{0.96}\text{Ca}_{1.04}\text{TiNbO}_{6.98}$ in oxidizing atmosphere [28]. On the other hand, some weight gain is exhibited by YST-1 and YST-2 samples after 500°C because of some rearrangement in the internal structure in both nitrogen and air atmosphere. Moreover, DTA also exhibits broad exothermic peaks in air after 500°C which further confirm the TG results. This can be explained because of order to disorder phase transitions in these samples after doping of Sr^{2+} for Y^{3+} . The conductivity plots of these samples also show prominent transition after 500°C in both the samples as shown in (figure 4.27) (discussed later). These transitions are prominent and show shifting towards higher temperature side which might be correlated with higher oxygen vacancy contents in these samples as compared to undoped sample. Moreover, in YST-2 sample no significant weight change is observed in air atmosphere signifying greater stability of this sample. YST-3 sample shows significant weight gain from 350°C to 900°C which is due to absorption of residual oxygen present in nitrogen. However, in YST-4 sample no weight change is observed from 350°C to 900°C showing higher stability in nitrogen atmosphere. Whereas, in air atmosphere sharp weight gain is observed from 500°C to

900°C which can be attributed to absorption of oxygen atoms from the air [38]. Moreover, the milled stoichiometric mixtures of Y_2O_3 and TiO_2 results in partially disordered phases, which are intermediate among the ordered pyrochlores and disordered fluorite structures. These partially disordered pyrochlores transform into the nearly ordered form around 800°C because of the oxygen re-arrangement [43]. A similar peak is obtained in YST and YST-4 samples in both air and nitrogen atmosphere nears 800°C showing, that order to disorder transition has taken place. The TGA of Ca doped samples i.e., YCT-1, YCT-2, YCT-3 and YCT-4 done in argon atmosphere are shown in figure 4.24.

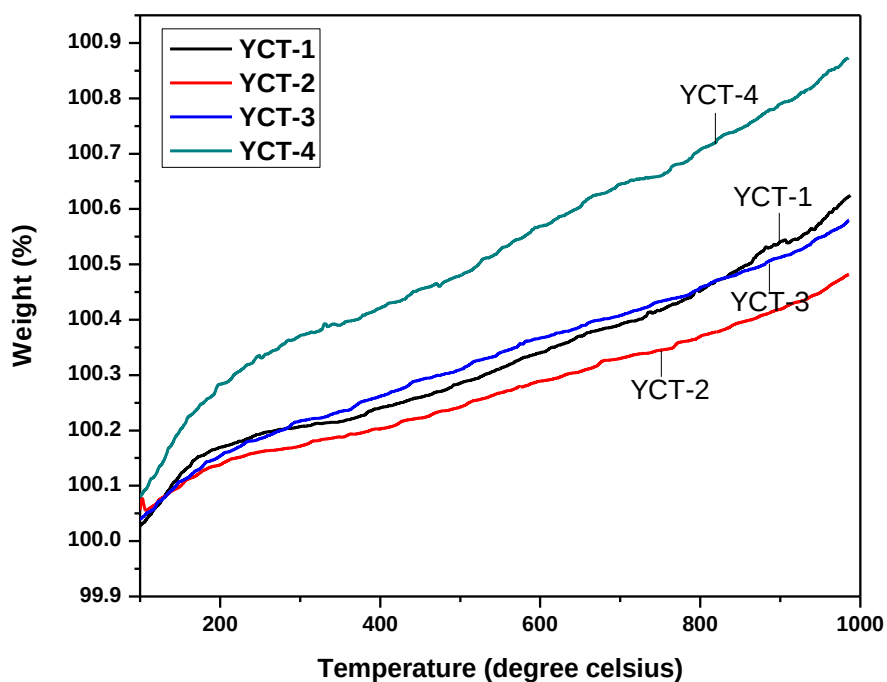


Figure 4.24: Thermo gravimetric analysis of YCT-1, YCT -2, YCT-3 and YCT-4 samples in argon atmosphere.

The weight gains observed in the present samples are mainly contributed due to some internal rearrangement and order to disorder transitions. The DTA plots of all the samples are shown in

figure 4.25. Initially, all the samples show broad endothermic hump followed by exothermic hump at nearly 800 °C. These events diminish with increasing concentration of dopants. The lack of TGA reports on these system prompt us to compare present results with ball milled synthesized samples. According to them, milled stoichiometric mixture of Y_2O_3 and TiO_2 result in partly disordered phases, which are intermediate among the ordered pyrochlores and disordered fluorite structures. These partly disordered pyrochlores transform into the nearly ordered form around 800 °C because of the oxygen rearrangement [43]. Interestingly, an exothermic kink is observed in YCT-4 sample at nearly 700 °C which is again manifestation of order to disorder transition in this sample.

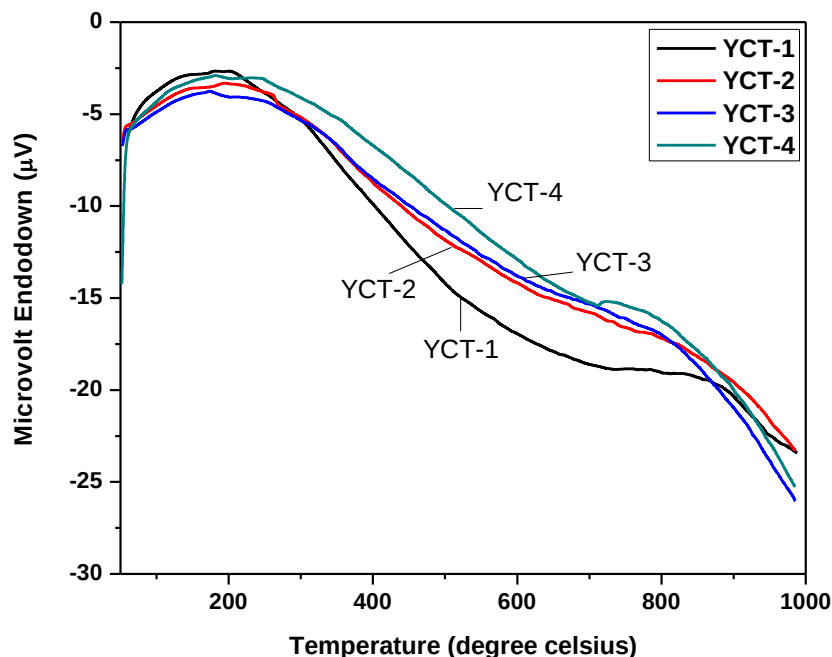


Figure 4.25: Differential thermal analysis of YCT-1, YCT -2, YCT-3 and YCT-4 samples in argon atmosphere.

4.1.6 Thermal expansion coefficient

Table 4.8 shows the TEC values of doped $\text{Y}_2\text{Ti}_2\text{O}_7$ and undoped samples. Most of the samples exhibit cubic symmetry, so no anomaly is observed in thermal expansion curve. However, higher TEC is observed in YT-2 sample. Basically, the TEC of the materials have a tendency to increase with the bond strength. Obviously, the presence of higher oxygen vacancies reduces the bond strength in YT-2 sample which leads to slightly higher TEC as compared to YT-1 sample. Moreover, the change in cation size (Ti^{4+} - Ti^{3+}) might also be playing role to enhance the TEC in YT-2 sample.

Table 4.8: Thermal expansion coefficient of YT-1, YT- 2, YCT-1 to YCT-4 samples.

Sample Name	YT-1	YT-2	YCT-1	YCT-2	YCT-3	YCT-4
TEC ($\times 10^{-6} \text{ K}^{-1}$)	8.36	8.39	8.42	8.53	8.54	8.44

In doped samples, the higher TEC is observed in YCT-2 and YCT-3 samples in comparison with YCT-1 sample. This can be attributed to the growth of minor orthorhombic CaTiO_3 phase along with major $\text{Y}_2\text{Ti}_2\text{O}_7$ phase. Since, TEC of the materials have a tendency to increase with decreasing bond strength so, the presence of minor orthorhombic CaTiO_3 phase has less bond strength in YCT-2 and YCT-3 samples which lead to slightly higher TEC as compared to YCT-1 sample. Whereas, in YCT-4 sample minor CaTiO_3 phase with monoclinic symmetry occurs along with $\text{Y}_2\text{Ti}_2\text{O}_7$ phase resulting in slight decrease in TEC of this sample in comparison with YCT-3 sample. The TEC value of the present sample is within the range of required values of SOFC [$8\text{-}13 \times 10^{-6} \text{ K}^{-1}$]. The TEC values of the present sample is less as compared to the reported values of pyrochlore and perovskites (CaTiO_3) i.e., $11.7 \times 10^{-6} \text{ K}^{-1}$. These anomalies can be explained on the basis of measuring temperature range. In the present investigation the TEC is

calculated in the temperature range from RT to 1000 °C. Whereas, in literature, TEC is measured upto the melting point of the samples [44].

4.1.7 Electrical conductivity measurement

The total resistance of the samples at various temperatures was determined from the point of intersection of the spectrum with the real axis and converted into conductivity using the following relation:

$$\sigma = \frac{l}{RA} \quad (4.1)$$

Where l is the thickness of the pellet and A is cross sectional area of the pellet.

With increasing temperature the resistance of the sample drops and conductivity increases which are manifestation of high temperature ionic conductors. As shown in figure 4.26, the conducting behavior of YT-1 sample generally shows linear behavior above 550 °C. Below 550 °C arrhenius plot of YT-1 sample shows lot of fluctuations. These fluctuations may be created due to competition between electronic and ionic conductors.

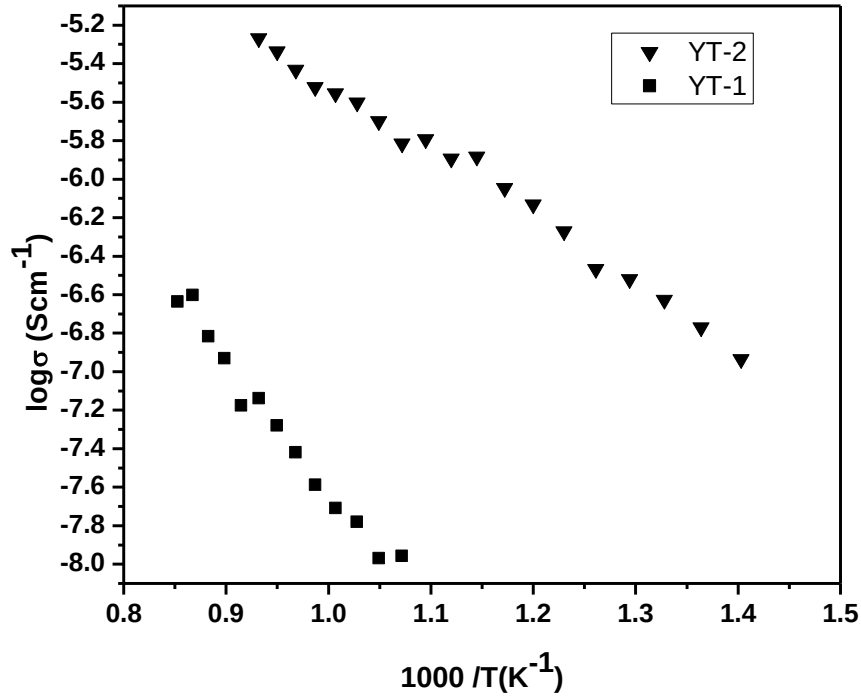


Figure 4.26: Arrhenius plot of YT-1 and YT-2 samples.

On the other hand, the fluctuations get subsidized in YT-2 sample and linear region extends up to nearly 350 °C. However, in YT-2 sample, a small disturbance in linearity is also observed between 550 °C and 600 °C. It may be attributed due to change of ordered pyrochlore to disordered pyrochlore phase. Similar results have also been reported for various pyrochlore samples [37]. The values of activation energy (E_g) for both the samples are calculated and summarized in table 4.9. The activation energy of YT-1 sample is slightly higher than YT-2 sample. It is also observed that conductivity of YT-2 sample is two orders of magnitude ($1.6 \times 10^{-5} \text{ Scm}^{-1}$) higher than YT-1 sample ($2.3 \times 10^{-7} \text{ Scm}^{-1}$). However, the conductivity of undoped pyrochlore has also been reported in same order as observed in YT-1 sample [1, 45, 46]. The conductivity difference between YT-1 and YT-2 samples can be explained on the basis of oxygen ion vacancies in YT-2 sample. Moreover, YT-2 sample possesses single phase with

higher density and lower porosity. The steep change in conductivity behavior of YT-2 as compared to YT-1 sample also indicates that this sample exhibits higher vacancies which provide the path for ion conduction. These results are also supported by the thermal analysis of these samples.

On the other hand, for Sr doped samples, it is observed that with increasing temperature the resistance of the sample drops and conductivity increases which are manifestation of high temperature ionic conductors. The $\log \sigma$ versus $1000/T$ plots for all samples are shown in figure 4.27 (a) and (b). The conducting behavior of YST sample generally shows linear behavior above 600°C. Below 600°C, at 550°C and 380°C arrhenius plot of YST sample shows fluctuations. YST-1 sample exhibits linear region up to 480°C with small disturbance in linearity among 460°C to 300°C. Similar results have also been reported for various pyrochlore samples [16]. The conductivity values for all the samples are calculated and summarized in table 4.9.

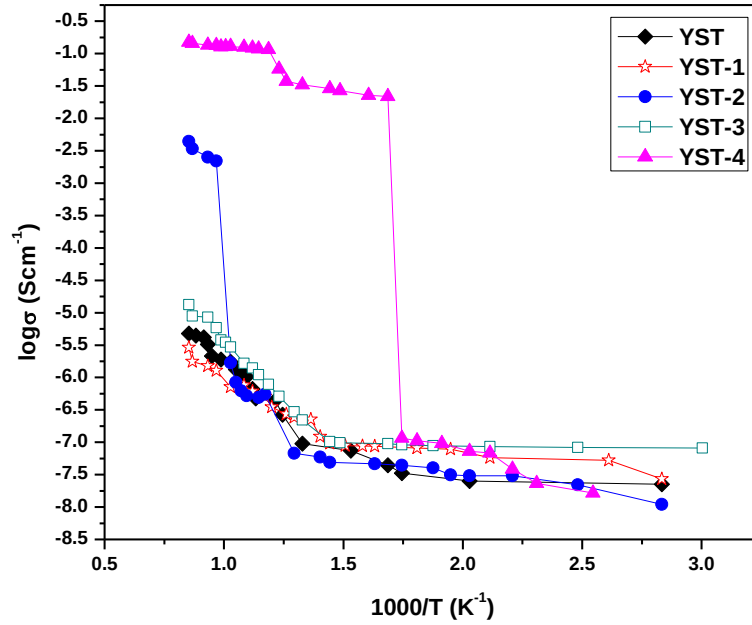


Figure 4.27 (a): Arrhenius plots of YST, YST-1, YST-2, YST-3 and YST-4 samples, respectively.

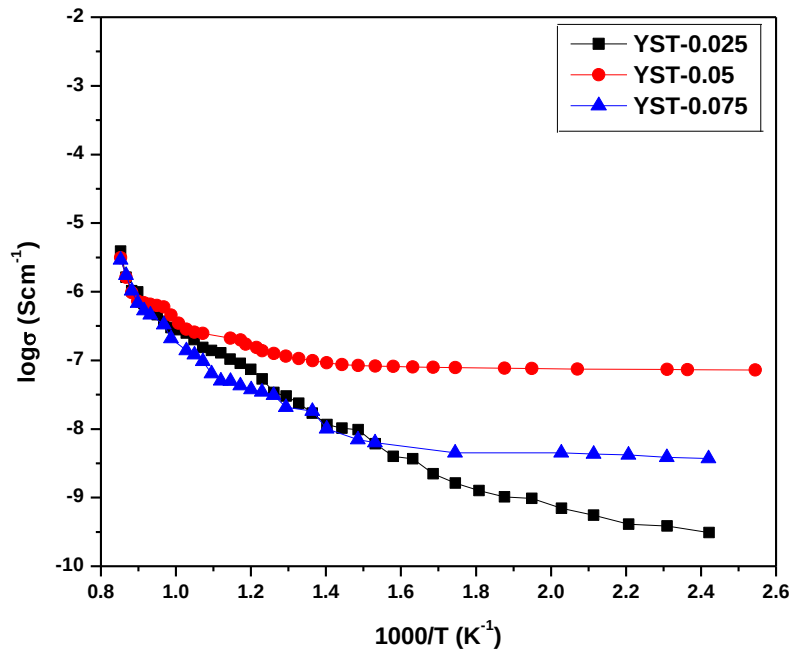


Figure 4.27 (b): Arrhenius plots of YST-0.025, YST-0.05 and YST-0.075 samples, respectively.

Table 4.9 (a): Electrical conductivity and activation energies of YT-1, YT-2, YCT-1 to YCT-4, samples.

Sample Label	YT-1	YT-2	YCT-1	YCT-2	YCT-3	YCT-4
Conductivity $\sigma_{900^{\circ}\text{C}}(\text{Scm}^{-1})$	2.31×10^{-7}	1.59×10^{-5}	3.16×10^{-6}	2.52×10^{-7}	2.69×10^{-7}	2.52×10^{-8}
E_a (eV)	0.61 (650 to 900°C)	0.30 (450 to 900°C)	0.26 (500 to 900°C)	0.27 (500 to 900°C)	0.27 (500 to 900°C)	0.30 (500 to 900°C)

Table 4.9 (b): Electrical conductivity and activation energies of YST, YST-1 to YST-4 samples.

Sample Name	Conductivity $\sigma_{900^{\circ}\text{C}}(\text{Scm}^{-1})$	$E_a > 750^{\circ}\text{C}$ (eV)	
		Total conductivity	Bulk and grain conductivity
YST	4.43×10^{-6}	0.43	0.40
YST-1	2.90×10^{-6}	0.36	0.33
YST-2	3.39×10^{-3}	0.22	0.19
YST-3	1.22×10^{-5}	0.30	0.29
YST-4	1.50×10^{-1}	0.13	0.11

The conductivity of undoped pyrochlore is of same order as observed in present YST and YST-1 samples and also in some reported data [1, 45-47]. Moreover, YST and YST-1 samples possess only single $Y_2Ti_2O_7$ phase which belongs with pyrochlore structure which is ordered anion-deficient. So, in both the samples conductivity comes out to be of similar order as shown in table 4.2. However, the conductivity decreases slightly in YST-1 sample. It might be associated with ordering and small unit cell volume induced by the Sr^{2+} substitution up to $x=0.1$. The density, FT-IR and XRD results also support increasing ordering in this sample which is contradictory to the reported work [16, 17, 22, 23]. Similar electrical conductivity results are also reported in doped pyrochlores [2]. The conductivity difference between YST-1 and YST-2 samples can be explained on the basis of transformation of $Y_2Ti_2O_7$ phase to $SrTiO_3$ phase as showed in our XRD results. It is well documented in literature that the $SrTiO_3$ phase has higher ionic conductivity than pyrochlore system. Additionally, in present system, charge compensation might be taking place mainly via oxygen vacancy formation rather than via generation of any positive charge carriers [47]. The doping of Sr^{2+} enhances the order-disorder transition and transition become prominent with doping due to intrinsic electronic disorder. At high temperature, due to more lattice vibrations in the crystal structure order-disorder transitions will take place where electrons can easily hop from one cationic site to another. Evidently, phase transition is clearly observed from 700°C to 800°C in arrhenius plots of YST-2 and YST-4 samples as shown in figure 4.27. Moreover, another phase transition from 320°C to 300°C at lower temperature range in YST-4 sample is observed. This can be correlated with higher doping of Sr which exhibits two fold effects on pyrochlore ($Y_2Ti_2O_7$) systems i.e., $Y_2Ti_2O_7$ phase reduces at the cost of $SrTiO_3$ phase and intrinsic electronic disorder via charge compensation. Therefore, the order of conductivity changes from $3.39 \times 10^{-3} \text{ Scm}^{-1}$ for YST-2 to $1.50 \times 10^{-1} \text{ Scm}^{-1}$

for YST-4 at 900°C. The activation energy can be calculated from the slope of arrhenius plot. In present case, the activation energy lies between 0.43-0.13 eV as given in table 4.9. The observed conductivity measurements of various compositions are in good agreement with activation energy trend. Similar observations have been reported in various $\text{Bi}_4\text{V}_{2-x}\text{Ti}_x\text{O}_{11-\delta}$ ($0 \leq x \leq 0.4$) based systems [48]. However, ionic conductivity decreases from $3.39 \times 10^{-3} \text{ Scm}^{-1}$ for YST-2 sample to $1.22 \times 10^{-5} \text{ Scm}^{-1}$ for YST-3 sample due to the presence of crack in the sample as shown in figure 4.27 (a and b) though the measurement was done on several samples. Beside this, it is seen that for YST-4 sample, the conductivity changes drastically from $1.22 \times 10^{-5} \text{ Scm}^{-1}$ for YST-3 to $1.50 \times 10^{-1} \text{ Scm}^{-1}$ for YST-4. This change can be attributed due to increase of SrTiO_3 phase relative to $\text{Y}_2\text{Ti}_2\text{O}_7$ phase as shown in XRD in earlier section. In addition to this, for YST-3 sample, we have observed nearly same volume fraction of SrTiO_3 and $\text{Y}_2\text{Ti}_2\text{O}_7$ phases i.e., 49% and 52% respectively. Because of this, the ionic and electronic conduction both have become dominating factor which has caused higher scattering [49]. This may lead to decrease in overall conductivity of sample. Moreover, TGA experiment reveals steep change in weight of YST-4 sample in air showing that this sample exhibits higher vacancies which provide path for ion conduction. In addition to this, the $\log \sigma$ versus $1000/T$ plots for all Ca doped samples i.e., YCT-1, YCT-2, YCT-3, YCT-4 is shown in figure 4.28. The conducting behavior of YCT-1 sample shows three transitions. The transitions at 350 °C and 540 °C might be attributed to extrinsic to intrinsic transition and at 700 °C and is due to ordered to disordered phase in these systems. The extrinsic to intrinsic transitions are extended to the higher temperature range in other samples as compared to YCT-1 sample. The conducting behavior of YCT-2 sample shows linear behavior above 500 °C and extended up to 600 °C in YCT-3 sample. Below 500 °C, at 300 °C arrhenius plot of YCT-2 sample shows fluctuations. YCT-4 sample exhibits linear region up to 900 °C

showing greater stability of this sample. Similar results have also been reported for various pyrochlore samples [17]. The conductivity values for all the samples are calculated and summarized in table 4.9.

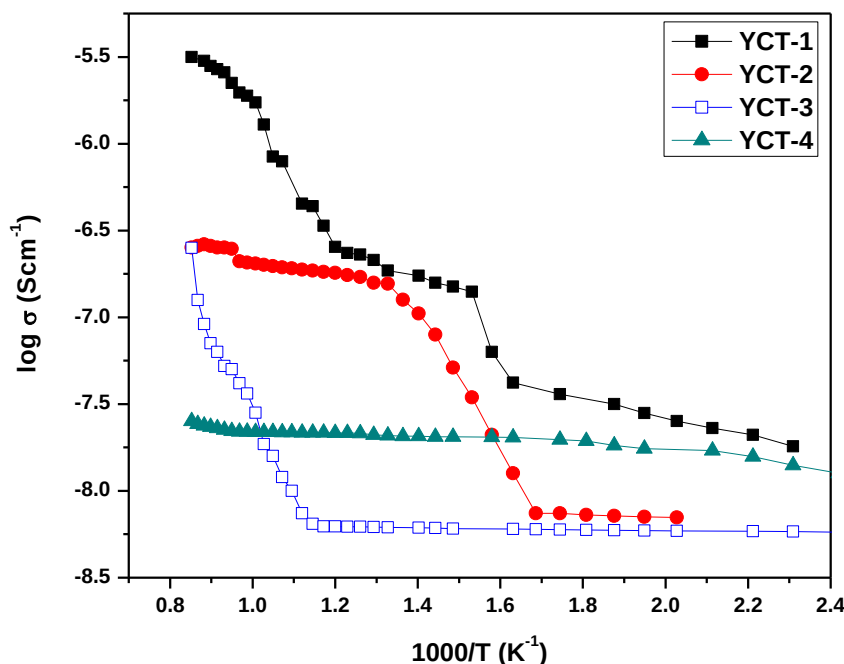


Figure 4.28: Arrhenius plots of YCT-1, YCT-2, YCT-3 and YCT-4 samples.

It was observed by Kramer et al. [50] that Ca-doping on the “A” cation sublattice was found to increase the ionic conductivity by as much as two and half orders of magnitude. In other words, ionic conductivity increases initially with increase in dopant concentration of Ca^{2+} on A-site but at higher doping level; there is tendency of saturation of ionic conductivity. In YCT-1, the conductivity is higher than YCT-4 where the order of conductivity decreases by two orders of magnitude. In other words, doping of Ca^{2+} on A-site first increases the ionic conductivity in YCT-1 ($x = 0.1$), which gets saturated for YCT-2 ($x = 0.2$), YCT-3 ($x = 0.3$). It further drops by two orders for YCT-4 ($x = 0.4$). The decreasing trend in conductivity can be explained on the

basis of the volume fraction of perovskite phase (CaTiO_3). Moreover, the relative density of YCT-1 is more as compared to the other three samples. In other words, by increasing the concentration of Ca in $\text{Y}_2\text{Ti}_2\text{O}_7$, there is a phase change, the change in phase in solid crystals create hurdles in the anionic conduction. So at lower concentration of Ca ion doping maintain the single phase in $\text{Y}_2\text{Ti}_2\text{O}_7$ and conduction increases due to generation of oxygen ion vacancies. The activation energy can be calculated from the slope of arrhenius plot. In present case, the activation energy lies between 0.26-0.30 eV as given in table 4.9.

The observed conductivity measurements of various compositions are in good agreement with activation energy trend. Moreover, the solid solution solubility in both the cases i.e., Sr^{2+} or Ca^{2+} is same.

4.2 Sr^{2+} and Ca^{2+} doped lanthanum orthoniobate systems

In this series, the doping of $\text{Sr}^{2+}/\text{Ca}^{2+}$ for LaNbO_4 was done. The structural, electrical as well as thermal properties of undoped as well as Sr^{2+} and Ca^{2+} doped LaNbO_4 composites have been investigated in this section. All samples are prepared by standard solid state reaction method and characterized by different techniques as described in experimental section of the thesis.

4.2.1 Physical properties

The resulting samples show good sinterability at 1300 °C and density obtained is greater than 90% of the theoretical density for undoped sample [51]. The relative density decreases as volume fraction of secondary phase $(\text{Sr}_{0.6}\text{La}_{0.4})(\text{Nb}_2\text{O}_6)$ increases as shown in table 4.10. The density of samples was calculated using mixture rule as follow:

$$\rho_{\text{theoretical}} = V_A \rho_A + V_B \rho_B \quad (4.2)$$

where V_A and V_B are the volume fraction of LaNbO_4 and $(\text{Sr}_{0.6}\text{La}_{0.4})(\text{Nb}_2\text{O}_6)$ for LNS series whereas for LNC series also V_A and V_B are the volume fraction of LaNbO_4 and

(Ca_{0.95}La_{0.05})Nb_{1.99}O₆ phases, respectively. Similarly ρ_A and ρ_B are the theoretical densities of LaNbO₄, (Sr_{0.6}La_{0.4})(Nb₂O₆) and LaNbO₄, (Ca_{0.95}La_{0.05})Nb_{1.99}O₆ phases, respectively. The experimental density of the sintered samples was calculated by mass/volume ratio of the sintered pellets. The volume fractions of the phases were calculated using X-ray diffraction patterns of these samples. It was observed that LNS-1, LNS-2, LNS-3 and LNS-4 samples exhibit lower densities than undoped LNS sample. The decrease in density of LNS-1, LNS-2, LNS-3, LNS-4 samples seems to be related to the presence of minor phase whose volume fraction increases with increase in concentration of Sr²⁺ dopant. In general, the minor phase gets segregated along the grain boundaries of the major phase which prevents the grain growth of major phase. Due to this reason, the porosity increases and density of the samples decreases. On the other hand, the physical appearance of the sample, particularly LNS series shows clear change in color with respect to Sr dopant. It is observed that the color of the samples change from cream to brown as the Sr content is increased from LNS-1 to LNS-4 as shown in figure 4.29. The change in color of the samples occurred due to variation in the volume fraction of both the phases as well as change in transition state of the transition metals. During high temperature sintering, the transition state may change as reported in many complex ceramic systems [51]. In contrast to this, no significant change in color is observed in the Ca doped samples.

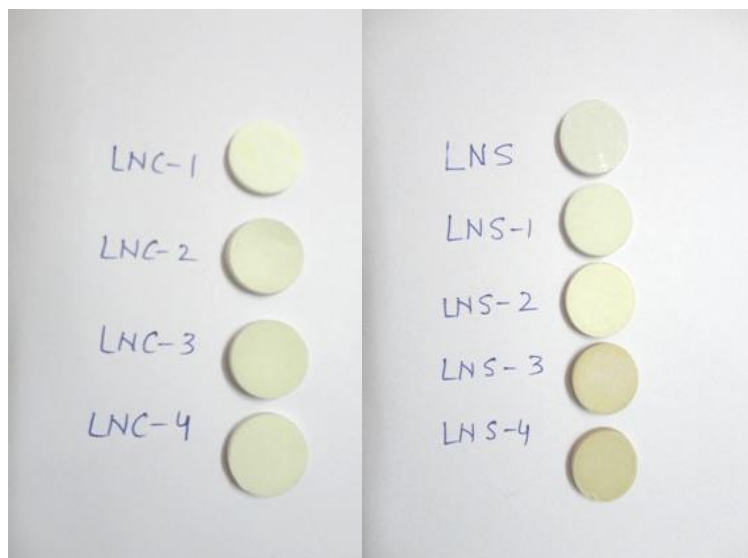


Figure 4.29: Physical appearance of LNS, LNS-1, LNS-2, LNS-3, LNS-4, LNC-1, LNC-2, LNC-3 and LNC-4 samples.

Table 4.10: Relative densities of LNS, LNS-1 to LNS-4, LNC-1 to LNC-4 samples, respectively.

Sample Name	LNS	LNS-1	LNS-2	LNS-3	LNS-4	LNC-1	LNC-2	LNC-3	LNC-4
Relative Density (%)	90	86	85	82	80	87	85	89	90

4.2.2 X-ray diffraction analysis (XRD)

XRD of LNS, LNS-1, LNS-2, LNS-3, LNS-4 and LNC-1, LNC-2, LNC-3 and LNC-4 samples are shown in the figure 4.30 (a) and (b), respectively. X-ray diffraction pattern of LNS sample shows the formation of single phase LaNbO_4 (ICDD Card No. = 00-022-1125). Most of XRD peaks are indexed with monoclinic phase of space group $I2/a$ [52]. However, some weak peaks could not be indexed with monoclinic phase. These XRD peaks match with other polymorphic state of LaNbO_4 phase. These peaks have been indexed to tetragonal structure of $(\text{LaNb}_3\text{O}_9)_{0.6667}$ phase with ICDD card number = 01-072-0040. This phase is commonly not been observed at room temperature [53]. However, in the present study, this might has formed due to liquid phase

sintering which is also observed in scanning electron micrographs of undoped sample (figure 4.32, discussed later). The retention of high temperature phase even at room temperature in this system is not reported so far. It is well reported in the literature that LaNbO_4 has many polymorphs [54]. On the other hand, the doping of Sr and Ca ($x = 0.1, 0.2, 0.3$ and 0.4) disrupt the LaNbO_4 phase and leads to formation of secondary phase $(\text{Sr}_{0.6}\text{La}_{0.4})(\text{Nb}_2\text{O}_6)$ (ICDD Card No.=01-082-1499) for LNS-1, LNS-2, LNS-3, LNS-4 samples and $(\text{Ca}_{0.95}\text{La}_{0.05})\text{Nb}_{1.99}\text{O}_6$ (ICDD Card No. = 01-071-6258) as minor phase for LNC-1, LNC-2, LNC-3, LNC-4 samples, respectively. The qualitative volume fraction of secondary phase was calculated using High Score plus software attached with x-ray diffraction instrument. The volume fraction of secondary phases increase with increasing content of SrO/ CaO in LaNbO_4 matrix. In other words, the XRD pattern of LNS-1, LNS-2, LNS-3, LNS-4 samples clearly shows the presence of $(\text{Sr}_{0.6}\text{La}_{0.4})(\text{Nb}_2\text{O}_6)$ as secondary phase. On the other hand, XRD pattern of LNC-1, LNC-2, LNC-3, LNC-4 samples clearly shows the presence of $(\text{Ca}_{0.95}\text{La}_{0.05})\text{Nb}_{1.99}\text{O}_6$ phase. The lattice parameters are calculated for undoped LNS sample whose value comes out to be $a = 5.77\text{\AA}$, $b = 11.62\text{\AA}$, $c = 5.34\text{\AA}$ which is slightly higher than the reported theoretical values [55]. This small variation in lattice parameters may be either due to coexistence of monoclinic and tetragonal phases or because of the presence of the tensile strain in the present sample. It is very difficult to obtain pure phase sample in these systems having Sr or Ca doping at higher concentration of dopant even after extensive grinding and intermediate heat treatments [56].

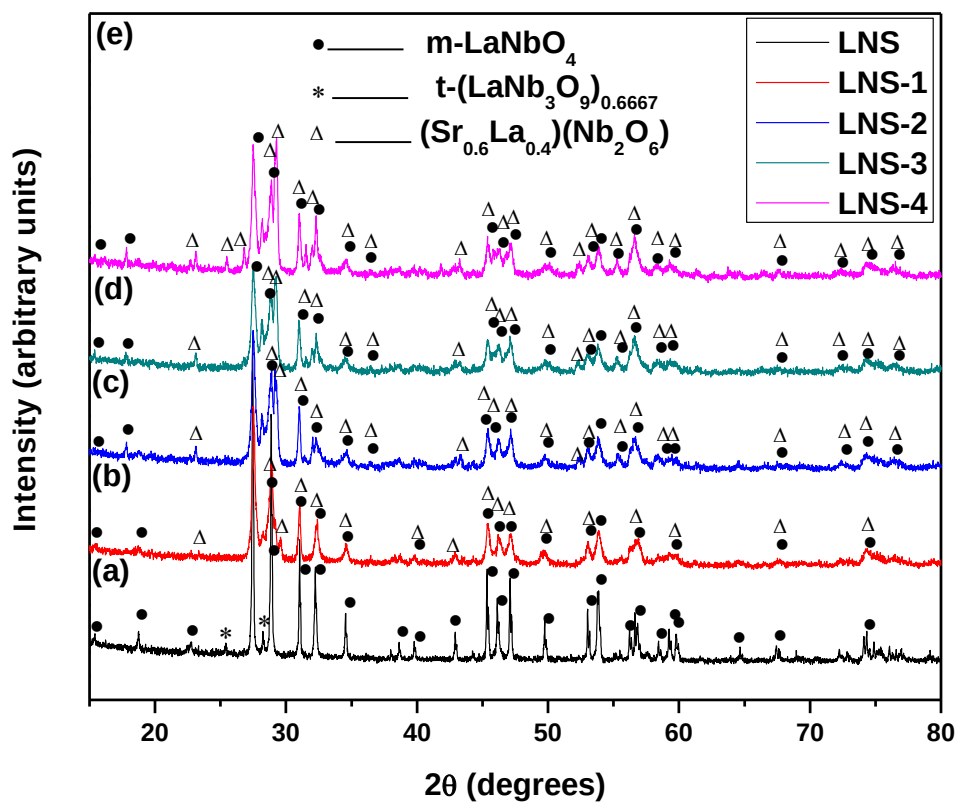


Figure 4.30 (a): X-ray diffraction pattern of (a) LNS, (b) LNS-1, (c) LNS-2, (d) LNS-3 and (e) LNS-4 samples.

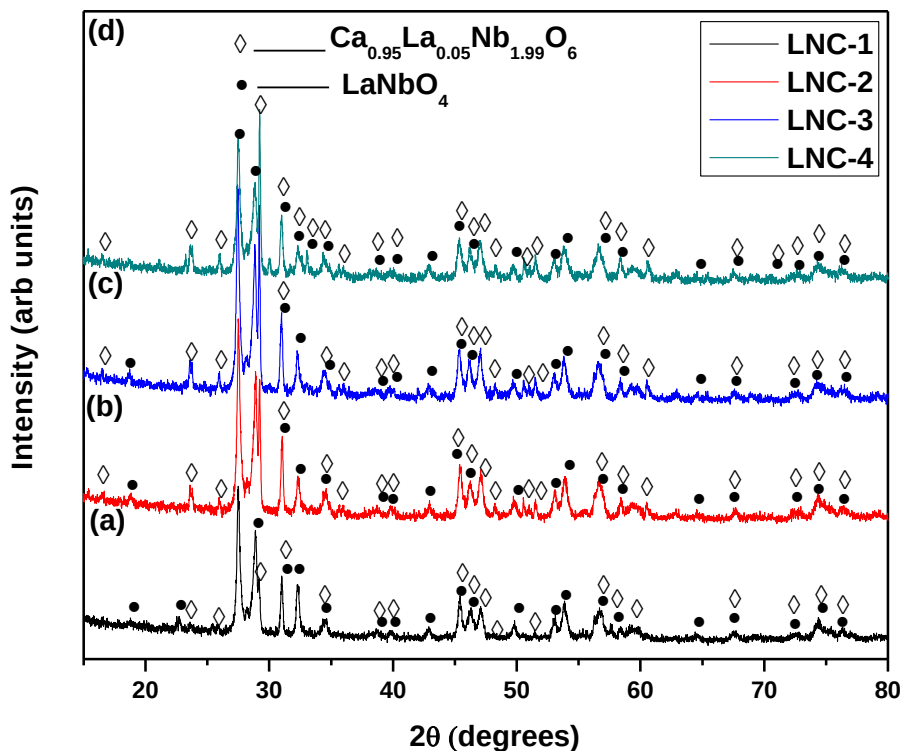


Figure 4.30 (b): X-ray diffraction pattern of (a) LNC-1, (b) LNC-2, (c) LNC-3 and (d) LNC-4 samples.

4.2.3 FT-IR analysis

FT-IR spectra of LNS, LNS-1, LNS-2, LNS-3, LNS-4 samples are shown in figure 4.31(a) and for LNC-1, LNC-2, LNC-3, LNC-4 samples are shown in figure 4.31(b). All the samples exhibit similar FT-IR spectra except some change in band intensity. A strong absorption peak in undoped LNS sample and weak absorption peak observed in other samples at 810 cm^{-1} can be attributed to the internal modes of the tetrahedral NbO_4 unit [57]. In addition to this, the appearance of absorption bands around 520 and 450 cm^{-1} is related to the Nb-O-Nb bending modes. These bands belong to La-O bonding [58]. Broadening observed around 600 cm^{-1} and 900 cm^{-1} band, after doping of Sr^{2+} in LNS, LNS-1, LNS-2, LNS-3, LNS-4 samples is a clear manifestation of weakening of La-O bond. It may be associated with formation of mixed bond of

La-O and Sr-O in these samples. Moreover, with increasing doping concentration the bands are shifted towards higher wave number with decreasing frequency. In other words, FT-IR spectra shows that fergusonite monoclinic phase LaNbO_4 is formed in all the samples and the host matrix of fergusonite becomes weak with addition of $\text{Sr}^{2+}/\text{Ca}^{2+}$ content in LNS sample to LNS-4 sample. The band broadening is more prominent in Ca-doped samples as compared to Sr-doped samples. These results are also in agreement with XRD results. The XRD pattern of Ca doped sample shows more broadening in peaks.

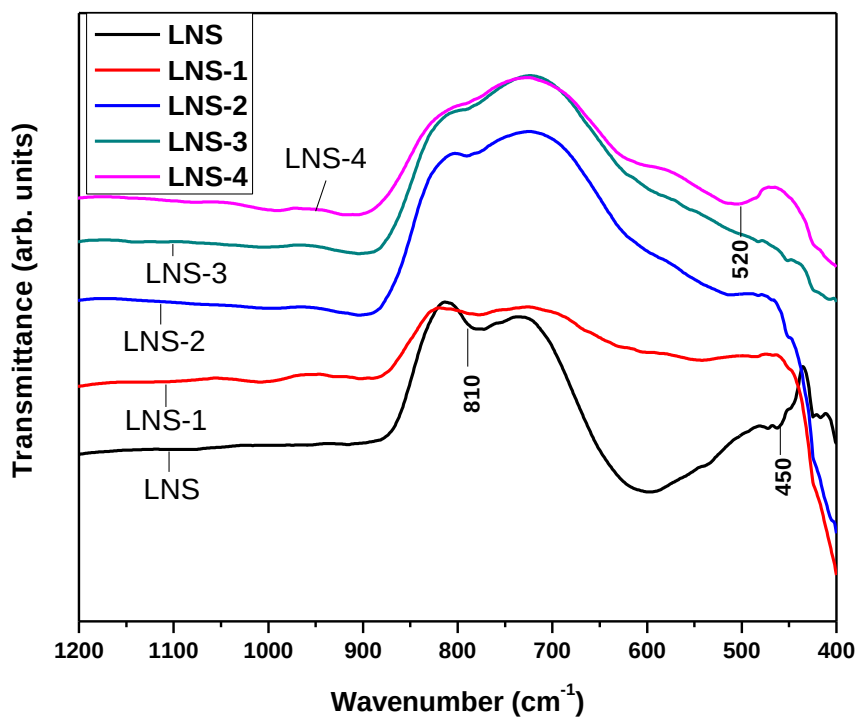


Figure 4.31 (a): FT-IR spectra of LNS, LNS-1, LNS-2, LNS-3 and LNS-4 samples.

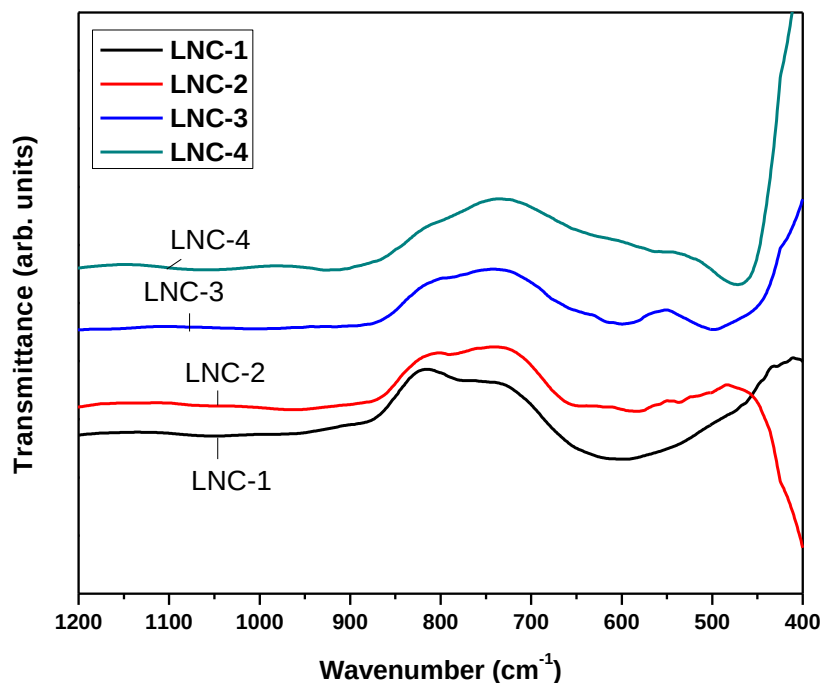


Figure 4.31 (b): FT-IR spectra of LNC-1, LNC-2, LNC-3 and LNC-4 samples.

4.2.4 Microstructural analysis

The SEM and optical micrographs of thermally etched surfaces of undoped LNS sample are shown in figure 4.32 and 4.33, respectively. Similarly, for doped LNS-4 sample it is shown in figure 4.34. These images provide information regarding grain size, shape, porosity and distribution of the crystallites. As indicated in figure 4.32 the grain size is non-uniform and irregular in shape. These results are contradictory to as reported earlier by Hsaio et al., [54]. However, the SEM shows the presence of two different morphologies of grains in undoped sample. The grain size varies between 2 μm to 20 μm (figure 4.32(a)). The surface structure appears to be decorated by small and coarse grains alongwith interconnected phase derived by solidification of liquid phase which is clearer in back scattered mode (figure 4.32(b)). This is because of quenching of liquid phase by the surrounding grains. Moreover, some grains exhibit

small internal cracks which may be due to the presence of strain. These cracks are transgranular in nature. As mentioned earlier, the XRD pattern of the undoped sample shows the shifting of peaks at lower angle which is manifestation of tensile strained lattice, thus causing surface cracks. The SEM analysis clearly indicates the presence of two phases having little variation in contrast as is evident in figure 4.32 (a, b). However, this slight variation in contrast in phases existing in grains and grain boundary may be of m-LaNbO₄ and t-(LaNb₃O₉)_{0.6667} as observed in X-ray analysis. Such type of contrast variation is because of the same chemical composition of phases. The back scattered micrograph clearly indicate that amount of elements present in the phases corresponding to grain and grain boundary is more or less same indicating the same chemical composition of both phases. In order to confirm it the sample was visualized under polarized light. The bright field and dark field micrograph taken under polarized light using polarizer and analyzer is shown in figure 4.33. The shining phases existing in dark field micrograph (figure 4.33 (b)) which are along the grain boundary correspond to tetragonal phase. This further confirms that sample LNS exhibits two different phases one monoclinic and other tetragonal having same chemical composition. On the other hand, the distributions of the grains are more non-uniform in LNS-4 sample as compared to undoped sample. It is observed that LNS-4 sample exhibit two crystalline phases with different morphology. The small circular white phase contains SrLaNb₂O₆ phase. Contrary to this, the dark larger grains (figure 4.34 (a) and (b)) represents monoclinic LaNbO₄ phase having domain structure. Similar results have also been reported for LaNbO₄ phase which exhibits ferroelastic behavior [59]. These results are also supported by X-ray diffraction of LNS-4 sample since XRD pattern clearly shows the presence of LaNbO₄ and SrNb₂O₆ phases. It is reported that as the ratio of La:Nb offset from 1:1, it leads to the formation of secondary phases [51]. The doped sample exhibit spherical agglomerated

morphologies with an average particle size $\sim 0.5 \mu\text{m}$ for SrNb_2O_6 phase. Similar observation has also been reported for CaNb_2O_6 and SrNb_2O_6 phases by Cho et al., [60]. In LNS-4 sample, addition of higher Sr on La-site results in increase in porosity and decrease the relative density. In other words, with increase of volume fraction of minor phase of $(\text{Sr}_{0.6}\text{La}_{0.4})(\text{Nb}_2\text{O}_6)$ as shown in XRD of LNS-1, LNS-2, LNS-3, LNS-4 samples, impedes the mass transportation and the sintering process leading to decrease in densities of these samples [23]. The EDS analysis was also done on the selected sample of doped and undoped LNS series. The qualitative analysis on two different phases existing in grain and at grain boundary for undoped LNS sample is shown in figure 4.35 and table 4.11. The undoped sample clearly shows the La:Nb ratio as 1:1. On the other hand, LNS-4 sample show the presence of LaNbO_4 and $(\text{LaSr})\text{Nb}_2\text{O}_6$ phases.

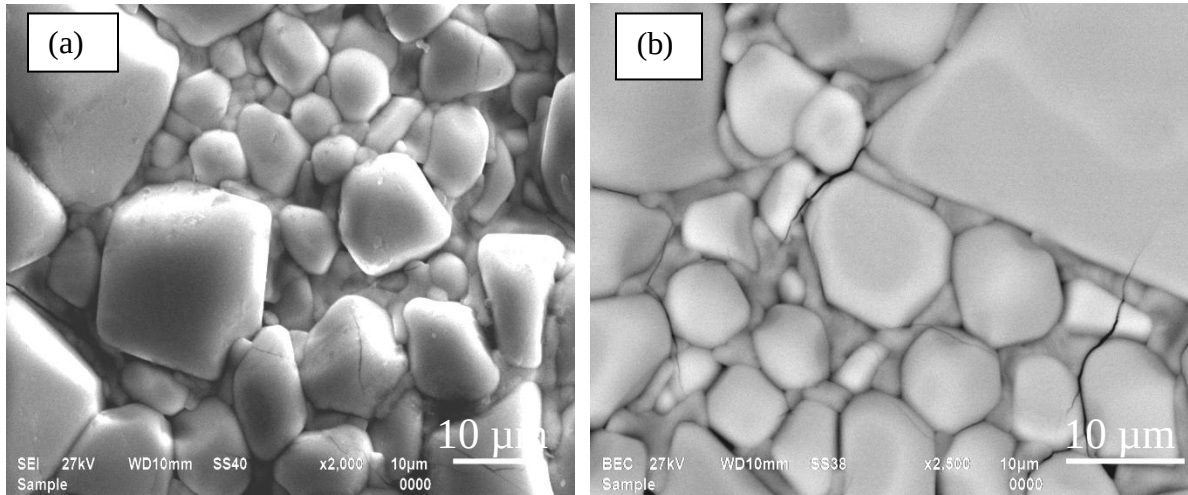


Figure 4.32: SEM of undoped LNS sample.

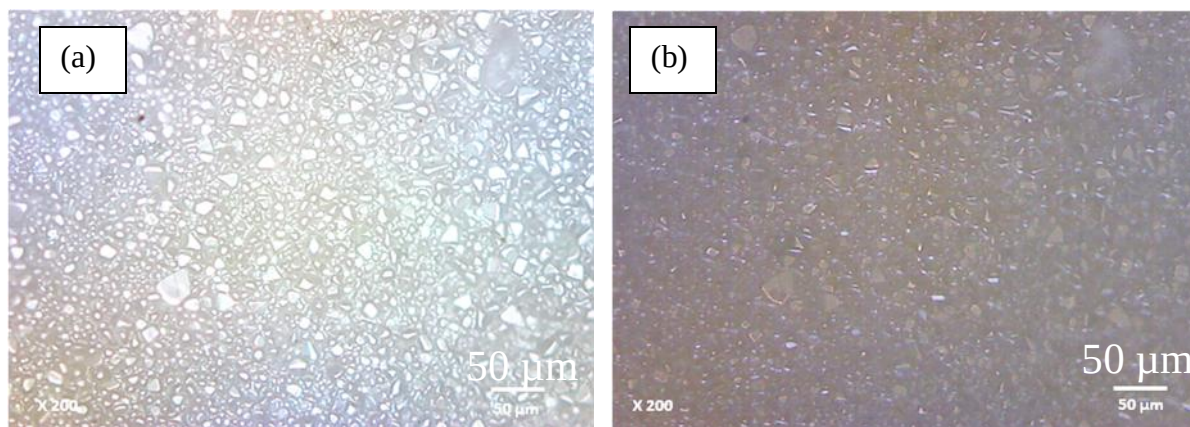


Figure 4.33: Bright field (a) and dark field (b) optical micrographs of undoped LNS sample.

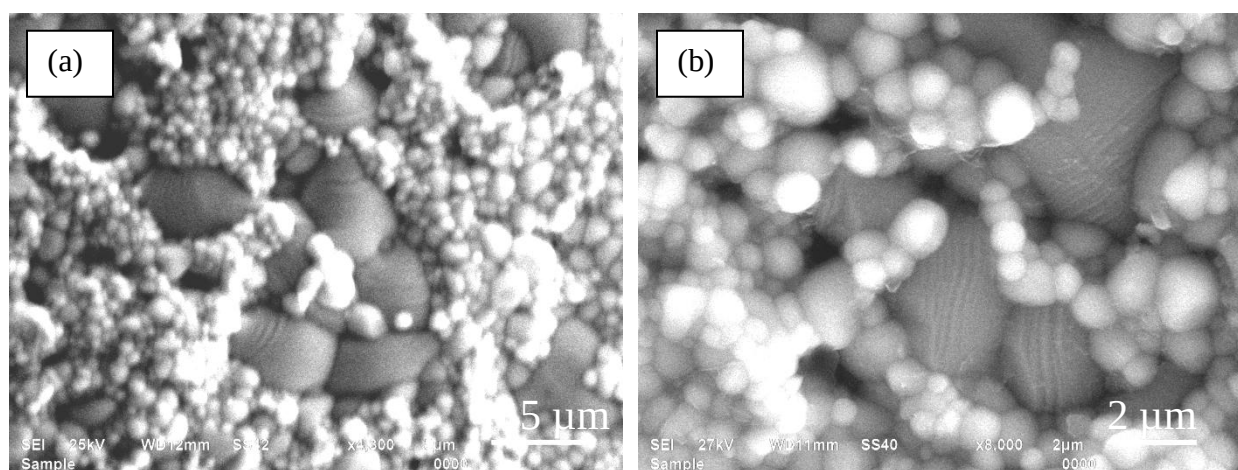
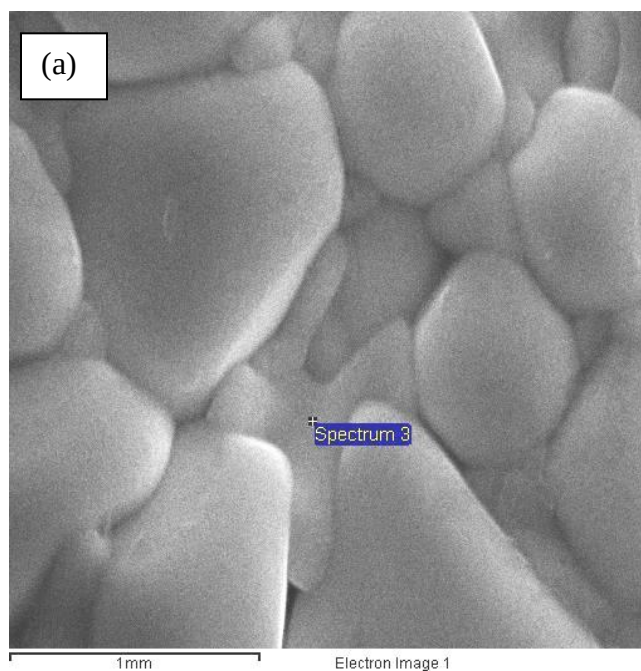


Figure 4.34: SEM of doped LNS-4 sample.



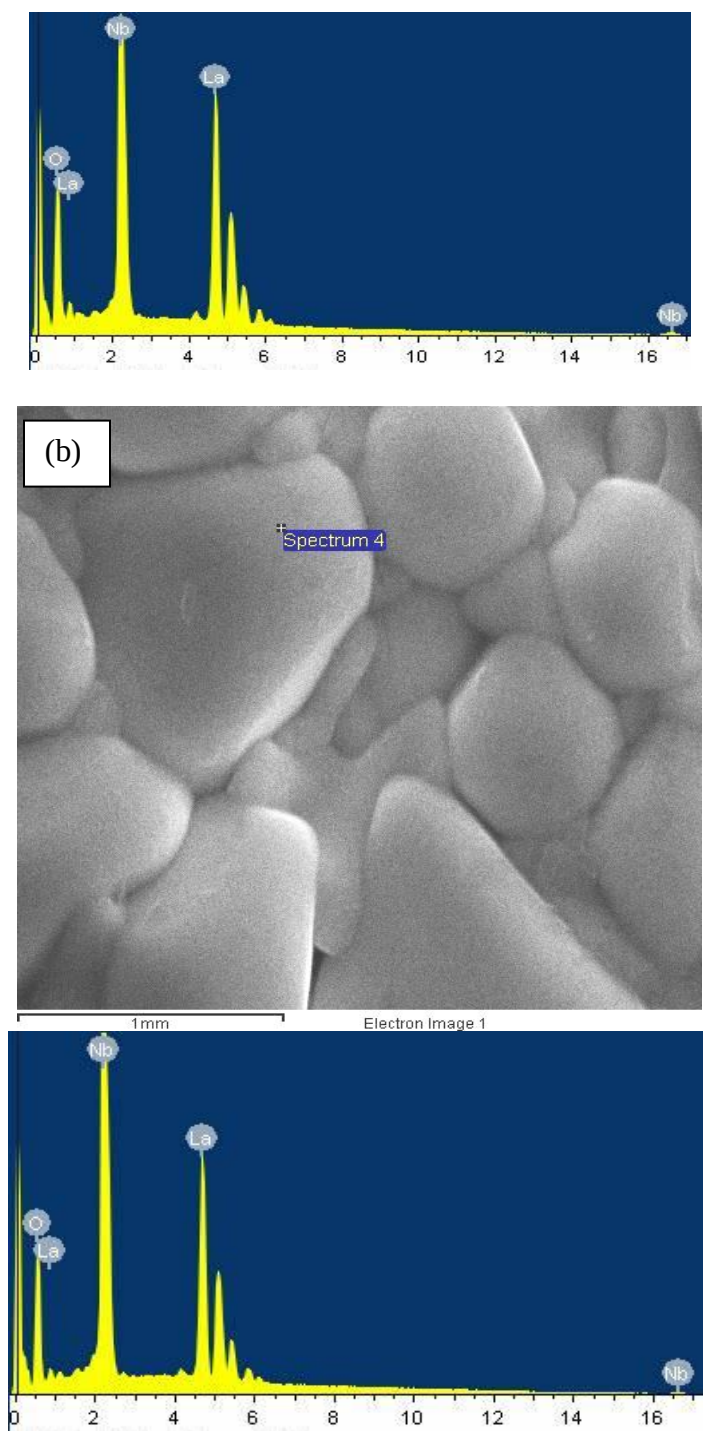


Figure 4.35: EDS analysis of undoped LNS sample.

Table 4.11(a): EDS analysis of undoped LNS sample (grain boundary).

Element	Weight (%)	Atomic (%)
O	24.70	70.34
Nb	30.60	15.00
La	44.70	14.66

Table 4.11(b): EDS analysis of undoped LNS sample (within grain).

Element	Weight (%)	Atomic (%)
O	23.30	68.12
Nb	36.37	18.31
La	40.32	13.58

4.2.5 Thermal analysis

Thermal gravimetric analysis of LNS, LNS-1, LNS-2, LNS-3, LNS-4, LNC-1, LNC-2, LNC-3 and LNC-4 samples done in nitrogen atmosphere is shown in figure 4.36 (a) and figure 4.36 (b). It is observed that undoped LNS sample shows weight gain of 0.5%, LNS-4 sample of 1.2%, LNC-4 sample of 0.85% in nitrogen atmosphere up to 1000 °C. The weight gain is observed in all the samples. However, the highest weight gain is observed for LNS-4 sample. Interestingly, undoped sample also shows the weight gain with respect to temperature. It can be attributed due to presence of Nb in mixed state which may get converted in lower valence state. Moreover, reducing atmosphere might get created in furnace during synthesis process at high temperature although reaction was performed in air. The conversion of Nb^{5+} to $\text{Nb}^{4+}/\text{Nb}^{3+}$ may lead to creation of some oxygen vacancies in the present system. These oxygen vacancies increase with doping of aliovalent cations such as $\text{Sr}^{2+}/\text{Ca}^{2+}$. Moreover, the increasing volume of secondary phase SrNb_2O_6 may increase the higher percentage of $\text{Nb}^{4+}/\text{Nb}^{3+}$ states of Nb leading to higher oxygen vacancies in the composite samples. It is also reflected in the TGA curve of the samples.

Mokkelbost et al., [59] have reported increase in oxygen vacancy concentration in LaNbO_4 by the partial substitution of divalent dopants for La^{3+} . The undoped/ doped particularly LNS and LNS-3 samples show the weight loss at 780 °C. This type of phenomena may lead to form more ordered LaNbO_4 phase [61] whereas, Ca doped sample could not show this type of behavior as shown in figure 4.36 (b). Additionally, the DTA measurement was performed on LNS sample to check the transformation of monoclinic to tetragonal phase in LaNbO_4 phase as reported by many researchers [62]. The DTA curve could not show the clear cut transformation temperature as shown in figure 4.36 (c). As discussed in section 4.2.2, the present sample exhibits the coexistence of monoclinic and tetragonal phase of LaNbO_4 even at room temperature. Hsaio et al., [54] have reported that the high temperature tetragonal phase could not be obtained even after changing the calcination conditions.

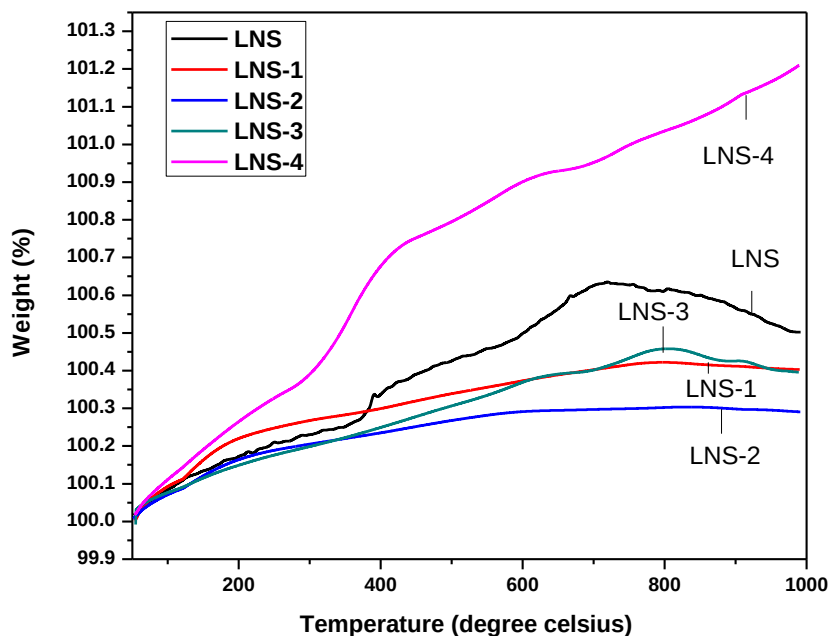


Figure 4.36 (a): Thermo gravimetric analysis of LNS, LNS-1, LNS -2, LNS-3 and LNS-4 samples, in nitrogen atmosphere.

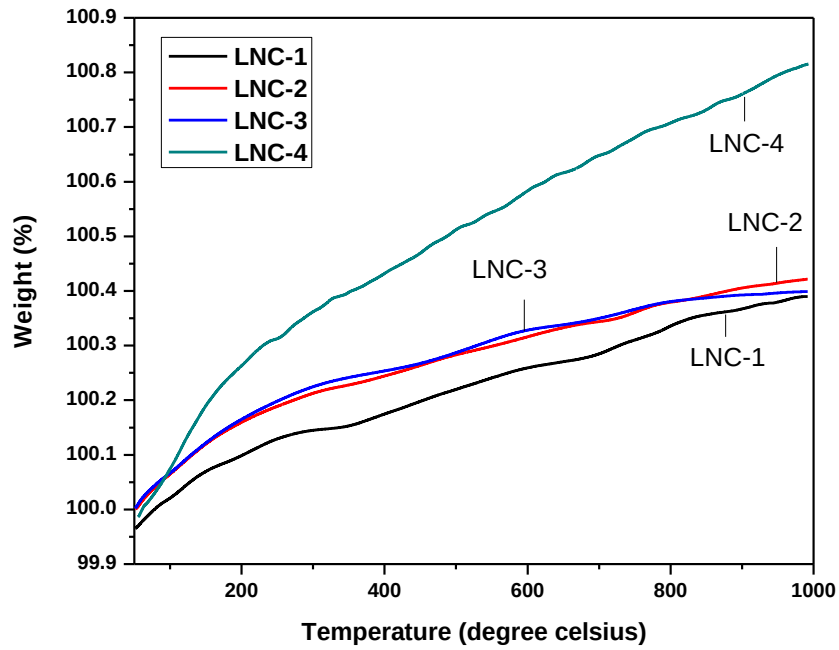


Figure 4.36 (b): Thermo gravimetric analysis of LNC-1, LNC -2, LNC-3 and LNC-4 samples, in nitrogen atmosphere.

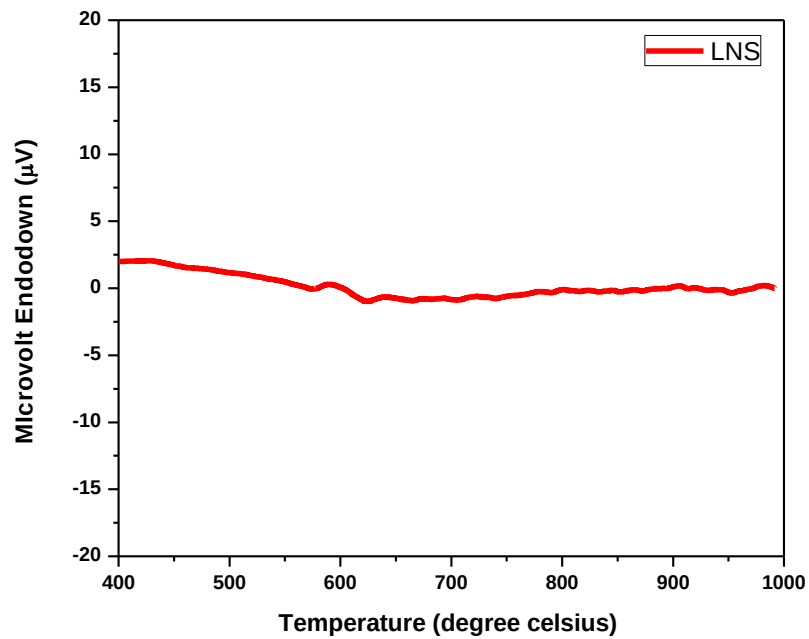


Figure 4.36 (c): Differential thermal analysis of LNS sample in nitrogen atmosphere.

4.2.6 Electrical conductivity measurement

The $\log \sigma$ versus $1000/T$ plots for all samples is shown in figure 4.37(a) to 4.37(c). Figures 4.37(d) and 4.37(e) show the variation of the real part (Z') of impedance with frequency at 500°C respectively. It is observed that magnitude of Z' decreases with increase in frequency indicating an increase in value of a.c. conductivity with rise in frequency [63]. In addition to this, the conducting behavior of LNS, LNS-1, LNS-2 samples show linear behavior up to 900°C whereas, LNS-3 sample exhibits linear region up to 650°C and LNS-4 sample exhibits linear region up to 850°C. On the other hand, LNC-1, LNC-2, LNC-3 and LNC-4 samples exhibit linear region up to 450°C, 550°C, 630°C, 640°C respectively with minor fluctuations. These minor fluctuations may be due to change in transport mechanism from electronic to ionic at this temperature. Teterin et al., [64] measured the conductivity of undoped rare-earth niobates and found electrical conduction to be dependent on both ions as well as electrons. Moreover, Haugrud et al., [65] found that if the doping concentration is below the solubility limit of the parent matrix then concentration of oxygen vacancies become independent of temperature and oxygen pressure. The conductivity values for all the samples are calculated and summarized in table 4.12. The data reveal that the conductivity of undoped LaNbO_4 is of the order of 10^{-7} Scm^{-1} and LNS-4 sample exhibits the highest conductivity of $1.01 \times 10^{-1} \text{ Scm}^{-1}$. A major conductivity difference observed in LNS-4 sample can be related to higher oxygen vacancies which provide path for ion conduction. Moreover, TGA experiment reveals steep change in weight of LNS-4 sample showing that this sample exhibits higher vacancies than other samples. However, nobody has reported conductivity of $1.01 \times 10^{-1} \text{ Scm}^{-1}$ at 900°C. This anomalous in conductivity behavior is because of presence of both the phases in optimized condition with higher oxygen vacancies. In contrast to this, Haugrud et al., [65] found proton conductivity of $\text{La}_{0.95}\text{Sr}_{0.05}\text{NbO}_4$ and $\text{La}_{0.99}\text{Ca}_{0.01}\text{NbO}_4$

system to be $1 \times 10^{-3} \text{ Scm}^{-1}$ and $9 \times 10^{-4} \text{ Scm}^{-1}$ in reducing atmosphere, respectively. In comparison to LNS systems, it is observed that LNC-1 sample exhibits higher conductivity by three orders of magnitude. This conductivity difference can be attributed to the fact that partial substitution of La^{3+} by Ca^{2+} introduces negative charge that is compensated by formation of oxygen vacancies resulting in increase in ionic conductivity [66]. Moreover, LNC-2, LNC-3, LNC-4 samples possess conductivity which comes out to be of similar order as shown in table 4.12. The activation energy can be calculated from the slope of arrhenius plot. In present case, the activation energy lies between 0.76-0.14 eV for LNS series and 0.38-0.25 eV for LNC series as given in table 4.12. The activation energy comes out to be amazingly low in LNS-4 sample which may have arised due to electronic conduction in this particular sample. The observed conductivity measurements of various compositions are in good agreement with activation energy trend. Similar observations have also been reported in various $\text{Bi}_4\text{V}_{2-x}\text{Ti}_x\text{O}_{11-\delta}$ ($0 \leq x \leq 0.4$) based systems also [48].

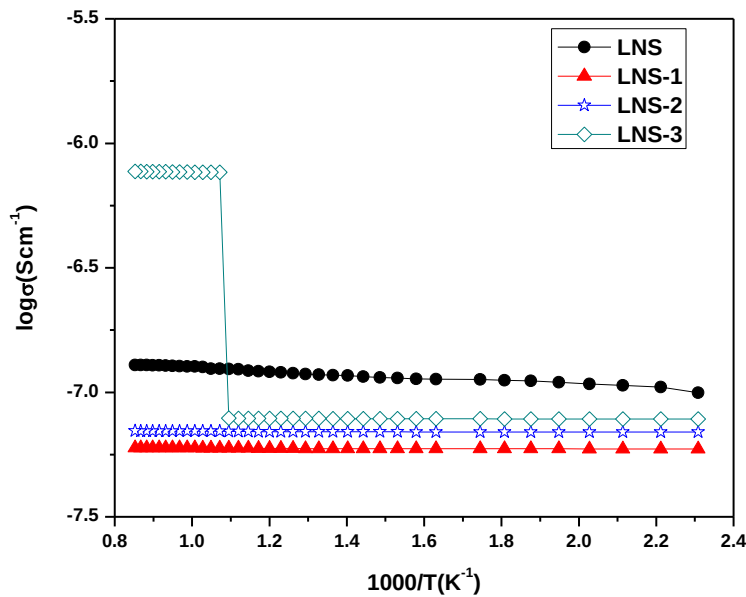


Figure 4.37 (a): Arrhenius plots of LNS, LNS-1, LNS-2 and LNS-3 samples.

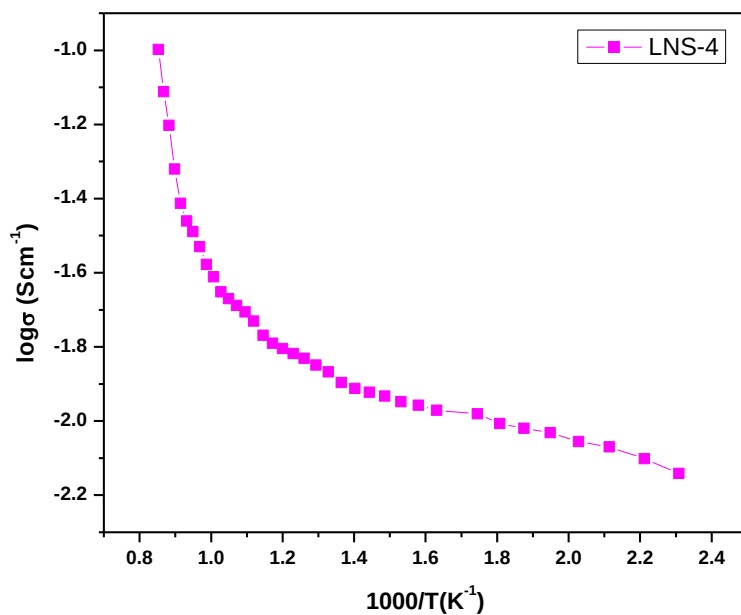


Figure 4.37 (b): Arrhenius plot of LNS-4 sample.

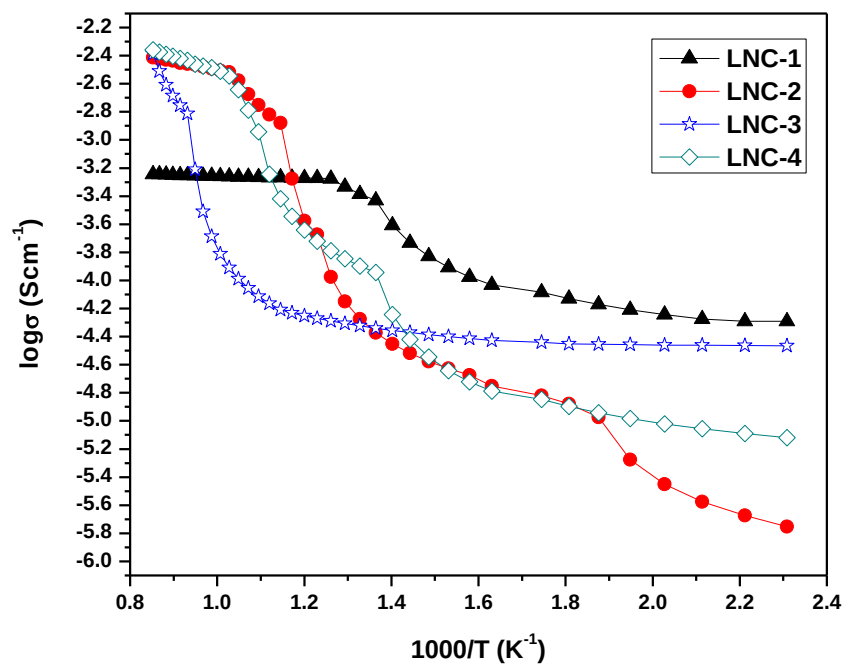


Figure 4.37 (c): Arrhenius plots of LNC-1, LNC-2, LNC-3 and LNC-4 samples.

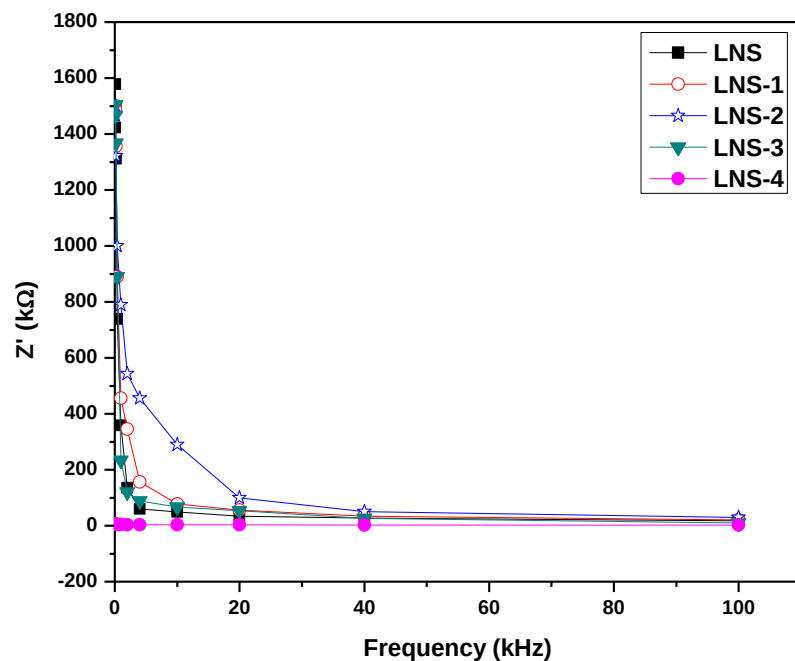


Figure 4.37 (d): Variation of real part of complex impedance (Z') of LNS, LNS-1, LNS-2, LNS-3 and LNS-4 samples.

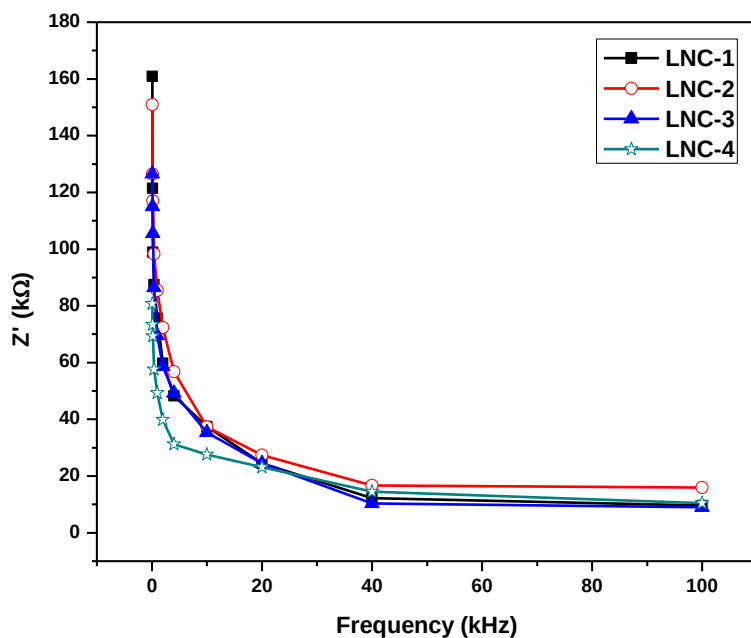


Figure 4.37 (e): Variation of real part of complex impedance (Z') of LNC-1, LNC-2, LNC-3 and LNC-4 samples.

Table 4.12: Electrical conductivity, activation energy and thermal expansion coefficient of LNS, LNS-1 to LNS-4, LNC-1 to LNC-4 samples, respectively.

Sample Label	Conductivity $\sigma_{900^{\circ}\text{C}}(\text{Scm}^{-1})$	$E_a > 750^{\circ}\text{C}$ (eV)	TEC ($\times 10^{-6} \text{ K}^{-1}$)
LNS	1.29×10^{-7}	0.56	8.11
LNS-1	5.99×10^{-8}	0.71	8.66
LNS-2	6.99×10^{-8}	0.76	8.22
LNS-3	7.71×10^{-7}	0.60	8.55
LNS-4	1.01×10^{-1}	0.14	8.38
LNC-1	5.71×10^{-4}	0.38	8.69
LNC-2	3.86×10^{-3}	0.29	8.70
LNC-3	4.12×10^{-3}	0.26	8.74
LNC-4	4.39×10^{-3}	0.25	8.55

4.2.7 UV visible analysis

The drastic change in conductivity, particularly LNS-4 sample, is unusual. The conductivity experiment was repeated several times for LNS-4 sample. The order of conductivity was found to be same. The anomalies were further confirmed by UV visible experiments on LNS, LNS-1, LNS-2, LNS-3, LNS-4 samples in reflectance mode. The calculated band gap of all the samples is given in table 4.13 and 4.14, respectively. Basically, the experimentally obtained absorption spectra of the samples comprises of two components. First one is of dispersed light due to scattering counted as absorbed light by the spectrophotometer and second one is the optical

absorption due to electronic transitions in the samples [67]. The undoped sample shows two band gaps viz. 4.62 and 3.49 eV. These bands are found to be very close to each another. The reported value of the band gap of LaNbO_4 is 4.8 eV [54]. The observation of two band gaps in undoped LNS sample confirms the coexistence of two forms of LaNbO_4 phase at room temperature as also observed in XRD pattern of undoped sample (figure 4.30 (b)). As the concentration of dopant is increased from LNS-1 to LNS-4 samples, the band gap corresponding to one phase gets stabilized [68]. However, the variation in second band gap is observed due to presence of secondary phase which is prominent in LNS-4 sample. The decrease in band gap might be the reason of higher conductivity of this particular sample. The drastic change in band gap has arisen due to higher oxygen vacancies in this sample. Moreover, the coexistence of two crystalline phases and their energy levels might also lead to decrease the band gap of LNS-4 sample. In case of Ca doped sample, the bands could not show any appreciable change in the band gap with dopant concentration. The conductivity behavior of Ca doped sample are also approximately constant i.e., $4.12 \times 10^{-3} \text{ Scm}^{-1}$. The UV visible results support the conductivity behavior of the present sample.

Table 4.13: Energy band gap of LNS, LNS-1, LNS-2, LNS-3 and LNS-4 samples, respectively.

Sample Name	Reflectance peak position (eV)	E_g (eV)	
LNS	4.62	3.49	
LNS-1	4.71	3.43	3.42
LNS-2	4.82	3.69	3.96
LNS-3	4.83	3.85	3.96
LNS-4	4.84	2.6	3.95

Table 4.14: Energy band gap of LNC-1, LNC-2, LNC-3 and LNC-4 samples.

Sample Name	Reflectance peak position (eV)	Eg (eV)
LNC-1	4.84	3.47
LNC-2	4.83	3.68
LNC-3	4.71	3.51
LNC-4	4.68	3.58

4.3 Sr²⁺ and Ca²⁺ doped yttrium orthoniobate systems

The present study deals with structural, electrical as well as thermal properties of undoped and doped YNbO₄ system. The main focus is on the effect of systematic doping of Sr and Ca for Y₂O₃ in YNbO₄ system. In this section, the structural, thermal and conductivity results are discussed.

4.3.1 X-ray diffraction analysis (XRD)

XRD of YNS, YNS-1, YNS-2, YNS-3, YNS-4, YNC-1, YNC-2, YNC-3 and YNC-4 samples are shown in the figure 4.38 (a) and 4.38 (b). X-ray diffraction pattern of YNS sample shows the formation of single phase YNbO₄ (ICDD Card No. = 01-072-2077). All the XRD peaks are indexed with monoclinic phase of space group I2/a [69]. Similar results have also been reported for A_{0.02}La_{0.98}NbO₄ (A= Ca, Sr or Ba) system after sintering at higher temperature [66]. On the other hand, the doping of Sr or Ca in Y_{1-x}Sr_x/Ca_x NbO₄ (x = 0.1, 0.2, 0.3 and 0.4) disrupt the YNbO₄ phase and leads to formation of SrNb₂O₆ (ICDD Card No. = 01-072-2088) and Sr₂Nb₂O₇ (ICDD Card No. = 01-070-9937) minor phases for YNS-1, YNS-2, YNS-3, YNS-4 samples and CaNb₂O₆ (ICDD Card No. = 01-071-2406) minor phase for YNC-1, YNC-2, YNC-3, YNC-4 samples, respectively. The volume fraction of secondary phases increase with increasing content of SrO/ CaO in YNbO₄ matrix as indicated in the table 4.15. In other words, the XRD pattern of

YNS-1, YNS-2, YNS-3, YNS-4 samples exhibits the presence of SrNb_2O_6 and $\text{Sr}_2\text{Nb}_2\text{O}_7$ as minor phases. It is found that YNbO_4 and SrNb_2O_6 phases with monoclinic structure are less symmetric than pyrochlore $\text{Sr}_2\text{Nb}_2\text{O}_7$ phase exhibiting orthorhombic structure. On the other hand, XRD pattern of YNC-1, YNC-2, YNC-3, YNC-4 samples shows the presence of CaNb_2O_6 phase. The sintered pellets of Ca doped YNbO_4 exhibits the cracks though the experiment was repeated several times. These cracks might have arised due to thermal expansion mismatch between YNbO_4 and CaNb_2O_6 phases since negative thermal expansion is reported in CaNb_2O_6 phase at particular temperature $\sim 900^\circ \text{C}$ [70]. Additionally, the XRD results of Ca doped samples are showing higher broadening in XRD peaks as compared to Sr doped samples as shown in figure 4.38 (c). The broadening of XRD peaks increases with increase in calcium concentration for YNC-1 and YNC-4, respectively. The XRD peak broadening can be explained on the basis of crystal structure of formed phases in Ca doped and Sr doped YNbO_4 samples. In case of Ca doped samples, formed crystalline phases are YNbO_4 and CaNb_2O_6 . The crystal structure of YNbO_4 is monoclinic. On the other hand, CaNb_2O_6 has orthorhombic crystal structure. However, Sr-doped YNbO_4 samples exhibit YNbO_4 , SrNb_2O_6 and $\text{Sr}_2\text{Nb}_2\text{O}_7$ phases. YNbO_4 and SrNb_2O_6 are monoclinic and the third phase $\text{Sr}_2\text{Nb}_2\text{O}_7$ exhibits ordered pyrochlore structure. Different crystal structure of YNbO_4 (monoclinic) and CaNb_2O_6 (orthorhombic) may also lead to higher peak broadening in the Ca-doped samples. Contrary to this, YNbO_4 and SrNb_2O_6 both are monoclinic and exhibit better homogeneity than YNC series samples. The lattice parameters calculated for undoped YNS sample are $a = 7.07 \text{ \AA}$, $b = 10.96 \text{ \AA}$, $c = 5.31 \text{ \AA}$ which is slightly higher than the reported lattice parameter values [55]. It clearly indicates the presence of tensile strain in the present samples. In other words, processing conditions play important role for crystalline phase formation in the present sample. Moreover, during processing the transition

metals (Nb) may get reduced from Nb^{5+} to $\text{Nb}^{4+}/\text{Nb}^{3+}$. This conversion may lead to the slight variation in lattice parameters in the present samples since $(\text{Nb}^{4+}/\text{Nb}^{3+})$ ionic radii are more than Nb^{5+} (0.69 Å) cations.

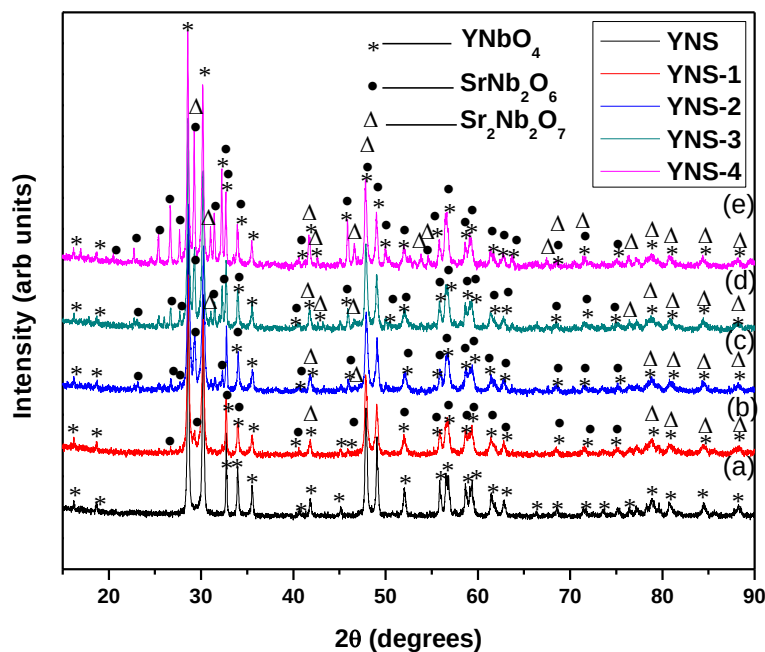


Figure 4.38 (a): X-ray diffraction pattern of (a) YNS, (b) YNS-1, (c) YNS-2, (d) YNS-3 and (e) YNS-4 samples.

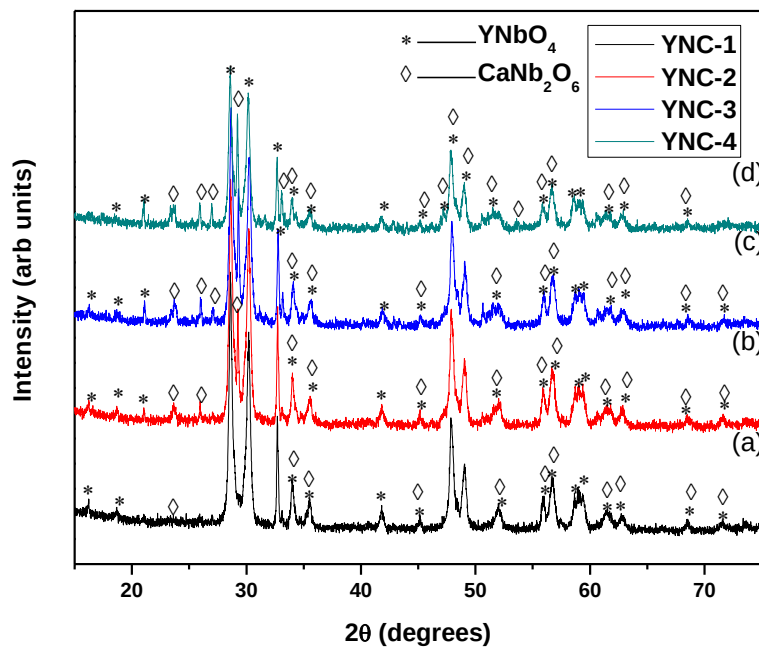


Figure 4.38 (b): X-ray diffraction pattern of (a) YNC-1, (b) YNC-2, (c) YNC-3 and (d) YNC-4 samples.

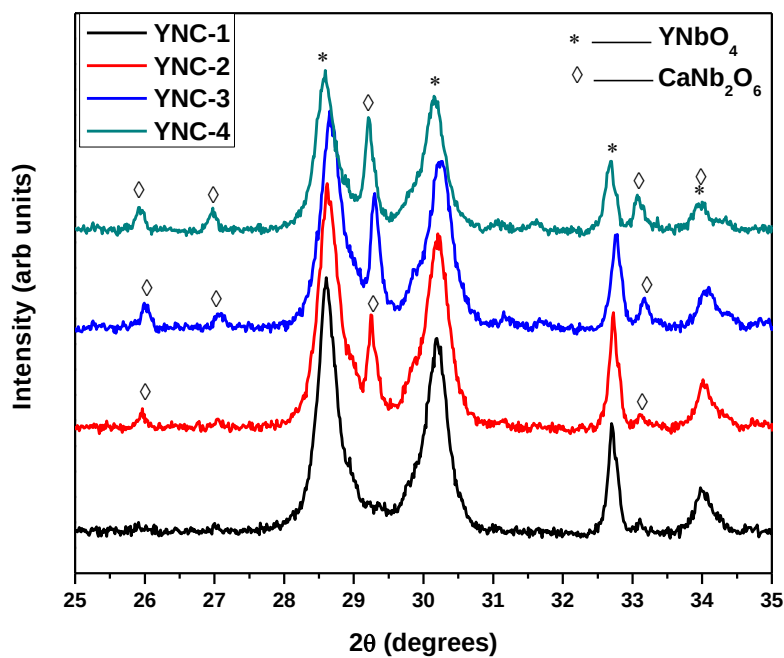


Figure 4.38 (c): Enlarged view of X-ray diffraction pattern of (a) YNC-1, (b) YNC-2, (c) YNC-3 and (d) YNC-4 samples.

Table 4.15: Volume fractions of YNbO_4 , SrNb_2O_6 , $\text{Sr}_2\text{Nb}_2\text{O}_7$, CaNb_2O_6 phases in YNS, YNS-1 to YNS-4, YNC-1 to YNC-4 samples.

Sample Name	Approximate Volume fraction (%) of crystalline phases			
	YNbO_4	SrNb_2O_6	$\text{Sr}_2\text{Nb}_2\text{O}_7$	CaNb_2O_6
YNS	100	-	-	-
YNS-1	76	12	12	-
YNS-2	51	26	23	-
YNS-3	51	27	22	-
YNS-4	42	26	33	-
YNC-1	87	-	-	13
YNC-2	77	-	-	23
YNC-3	73	-	-	27
YNC-4	64	-	-	36

4.3.2 FT-IR analysis

FT-IR spectra of YNS, YNS-1, YNS-2, YNS-3, YNS-4 samples are shown in figure 4.39 (a) and YNC-1, YNC-2, YNC-3, YNC-4 samples are shown in figure 4.39 (b). All the samples exhibit similar FT-IR spectra except some change in band intensity. A strong absorption peak in all the samples at 810 cm^{-1} can be attributed to the internal modes of the tetrahedral NbO_4 unit [57]. Moreover, absorption peaks at 806 cm^{-1} , 670 cm^{-1} , 597 cm^{-1} and 543 cm^{-1} appear in the monoclinic (M)- YNbO_4 structure [71]. The FT-IR spectrum of YNS, YNS-1, YNS-2, YNS-3, YNS-4, YNC-1, YNC-2, YNC-3, YNC-4 samples clearly shows some variations in their intensities and positions.

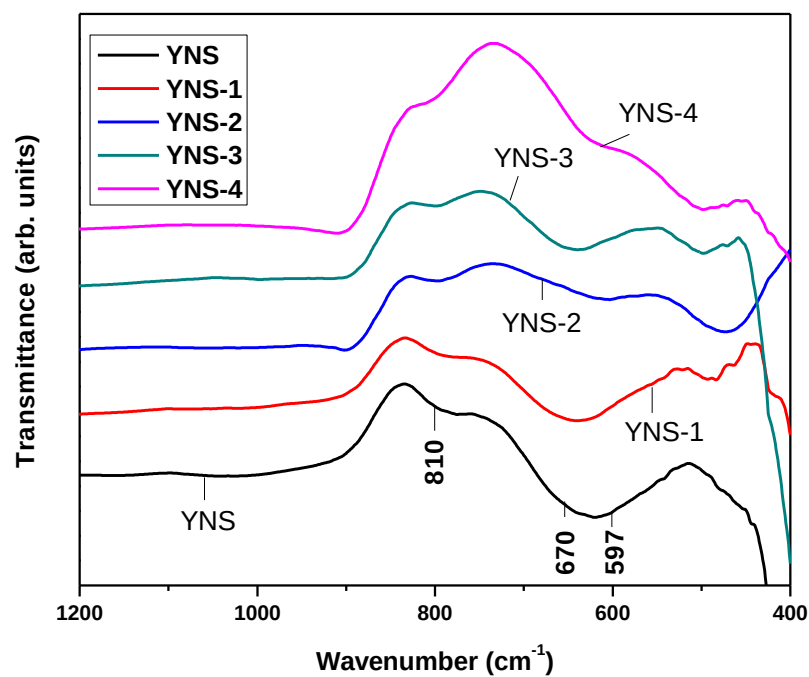


Figure 4.39 (a): FT-IR spectra of YNS, YNS-1, YNS-2, YNS-3 and YNS-4 samples.

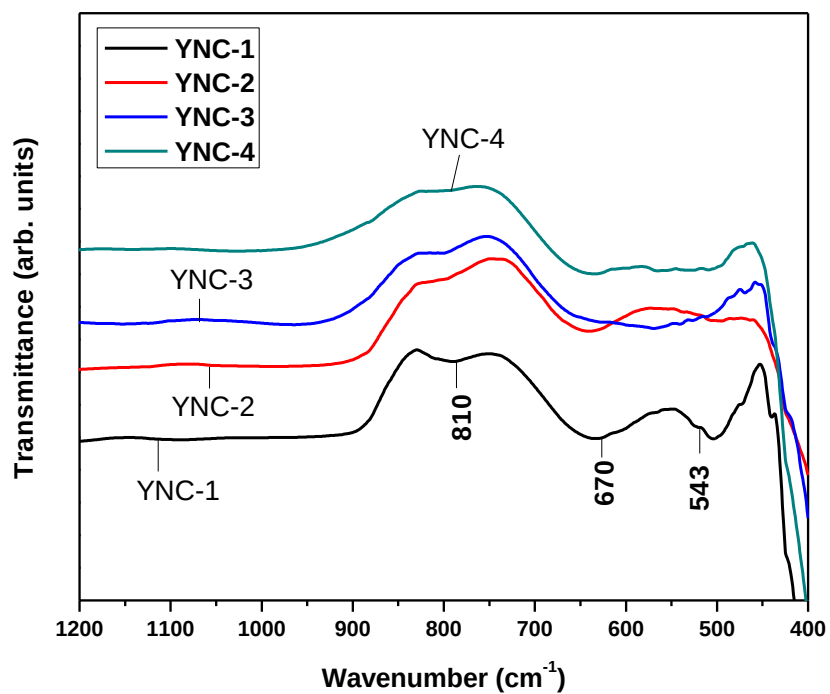
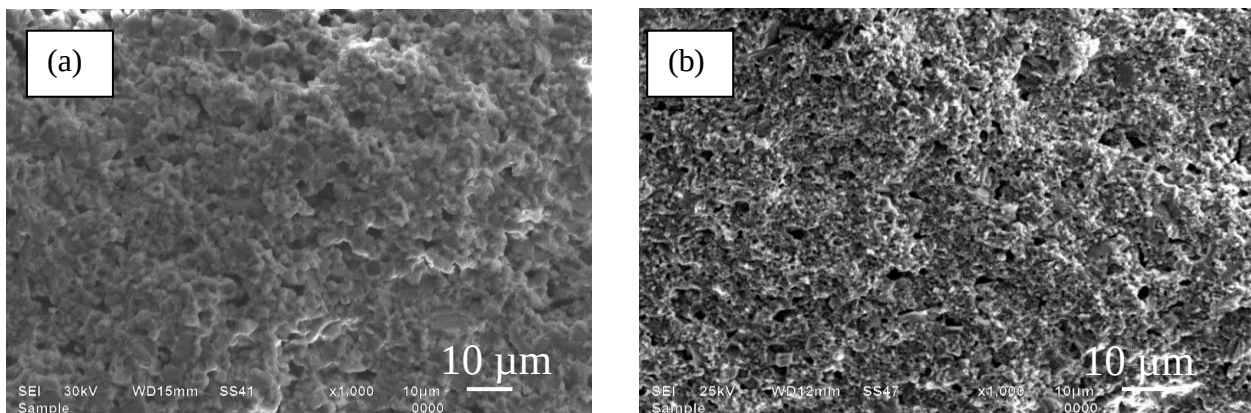


Figure 4.39 (b): FT-IR spectra of YNC-1, YNC-2, YNC-3 and YNC-4 samples.

These peaks become broader with doping of Sr^{2+} and Ca^{2+} in YNbO_4 matrix as clearly indicated from FT-IR spectra of all the samples. In addition to this, the appearance of absorption bands around 2400 cm^{-1} in all the samples can be attributed to the presence of Ca-O band in figure 4.39 (b). Moreover, peaks of lesser intensity are observed around 1450 cm^{-1} and 3600 cm^{-1} which are mainly due to CaO. In other words, FT-IR spectra indicated that host matrix of YNbO_4 becomes weak with addition of Sr^{2+} and Ca^{2+} content in YNS to YNS-4 samples and YNC-1 to YNC-4 samples, respectively.

4.3.3 Microstructural analysis

The SEM micrographs of fractured surfaces of undoped YNS and doped YNS-1, YNS-3, YNS-4 samples are shown in figure 4.40, respectively. In YNS sample, the distribution of the grains are non-uniform in all the samples. It is observed that all the samples are porous and pores are continuous as well as open. On the other hand, YNS-3, YNS-4 samples exhibit adjoining grains with very less porosity. In other words, in YNS-3 and YNS-4 samples, higher addition of Sr on Y-site results in increase in porosity as compared to other samples as also seen in table 4.15. This implies that with increase of volume fraction of minor phase of SrNb_2O_6 as shown in XRD of YNS, YNS-1, YNS-2, YNS-3, YNS-4 samples, impedes the mass transportation and the sintering process leading to increase in porosity of these samples [23].



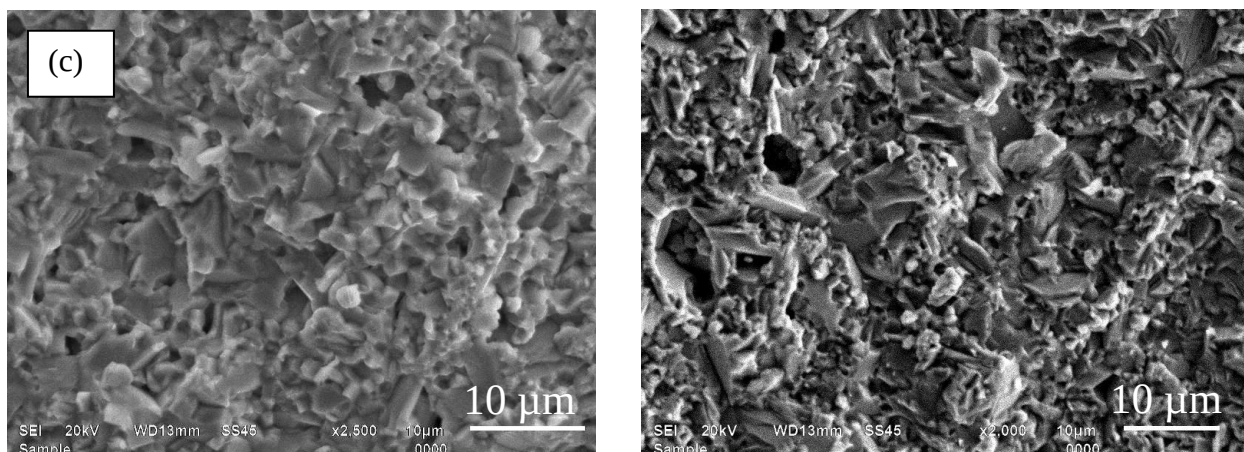


Figure 4.40: SEM of (a) YNS, (b) YNS-1, (c) YNS-3 and (d) YNS-4 samples, respectively.

4.3.4 Thermal analysis

Thermal gravimetric analysis of YNS, YNS-1, YNS-2, YNS-3, YNS-4, YNC-1, YNC-2, YNC-3 and YNC-4 samples done in nitrogen atmosphere is shown in figure 4.41 (a) and figure 4.41 (b). It is observed that undoped YNS sample shows weight gain of 0.68 %, YNS-2 sample of 0.55%, YNC-2 sample of 0.7%, YNC-3 sample of 0.65%. These changes in weight are observed up to 1000°C. Interestingly, undoped sample shows the highest weight gain with respect to other samples. It can be attributed due to presence of Nb in mixed state which got converted in lower valence state. It may have occurred due to reducing atmosphere which got created in furnace during synthesis process at sufficiently high temperature. It is also reported in some cases, particularly when transition metals are present as initial constituents. In addition to this, some unreacted metals got oxidized and increase the weight gain in all the samples as shown in figure 4.41 (a) and (b). On the other hand, the conversion of Nb^{5+} to $\text{Nb}^{4+}/\text{Nb}^{3+}$ may lead to create some oxygen vacancies in the present system [61]. These oxygen vacancies increase with doping of aliovalent cations such as $\text{Sr}^{2+}/\text{Ca}^{2+}$. However, the weight gain is very steep $\sim 200^\circ\text{C}$ in all the samples.

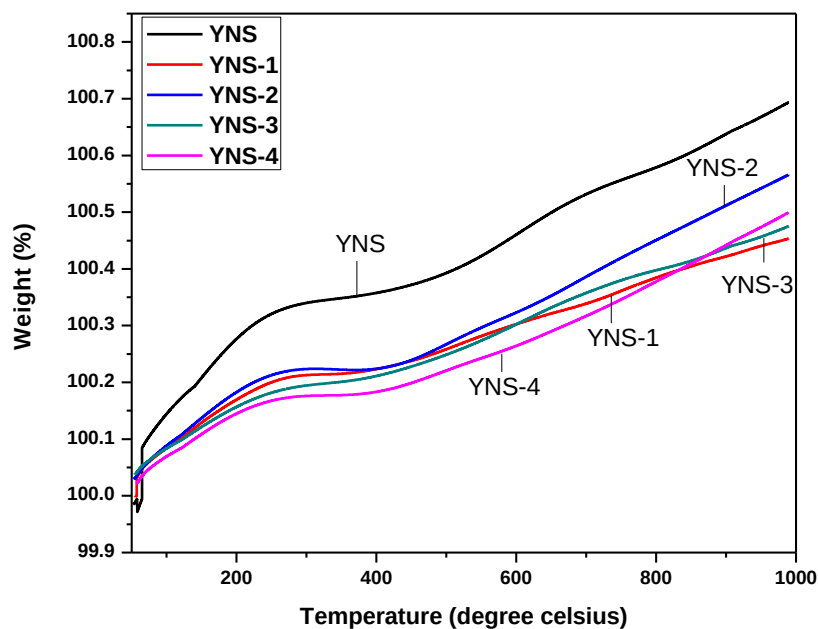


Figure 4.41 (a): Thermo gravimetric analysis of YNS, YNS-1, YNS -2, YNS-3 and YNS-4 samples in nitrogen atmosphere.

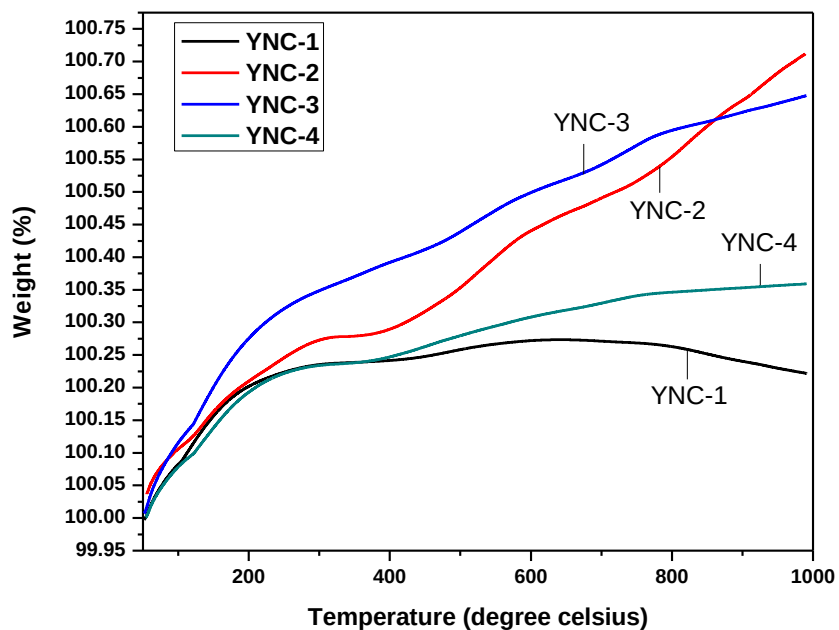


Figure 4.41 (b): Thermo gravimetric analysis of YNC-1, YNC -2, YNC-3 and YNC-4 samples in nitrogen atmosphere.

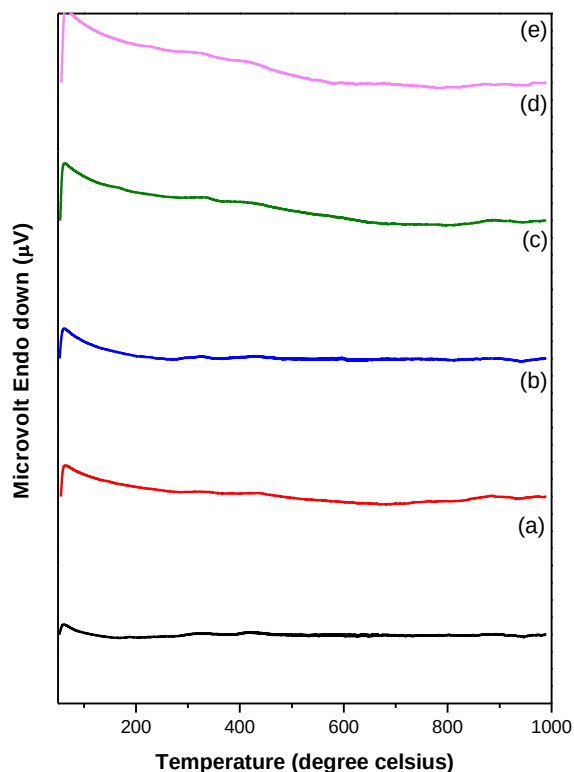


Figure 4.41 (c): Differential thermal analysis of (a) YNS, (b) YNS-1, (c) YNS -2, (d) YNS-3 and (e) YNS-4 samples in nitrogen atmosphere.

The DTA curves of all the samples could not show any remarkable thermal event up to 1000 °C as shown in figure 4.41 (c) and 4.41 (d). However Kriven et al., [72] have reported a phase transition at 450 °C in niobates. Contrary to this, Hsaio et al., [54] could not observe the tetragonal phase at high temperature evens after changing the processing conditions several times.

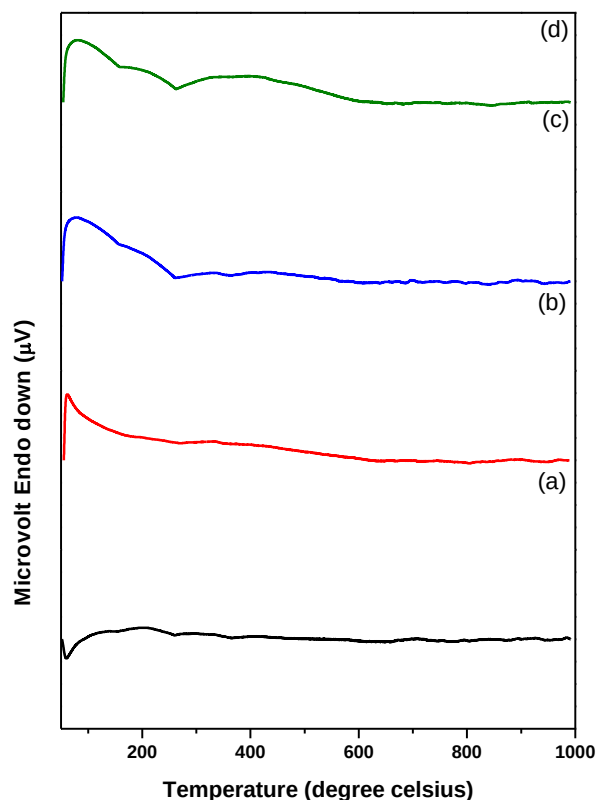


Figure 4.41 (d): Differential thermal analysis of (a) YNC-1, (b) YNC -2, (c) YNC-3 and (d) YNC-4 samples in nitrogen atmosphere.

4.3.5 Electrical conductivity measurement

The $\log \sigma$ versus $1000/T$ plots for all Sr- doped samples is shown in figure 4.42. The conductivity measurement could not be performed on the Ca-doped samples due to the presence of the cracks in the samples as mentioned in section 4.3.1. The conducting behavior of YNS, YNS-4 samples show linear behavior up to 900°C. Whereas, YNS-3 sample exhibits linear region up to 550°C and YNS-1 sample exhibits linear region up to 720°C. In addition to these, minor fluctuations are observed in all the samples. These minor fluctuations can be due to presence of mixed behavior of ions and electrons. Teterin et al., [64] measured the conductivity of undoped rare-earth niobates and found electrical conduction to be dependent on both ions as

well as electrons. Moreover, Haugrud et al., [65] found that if the doping concentration is below the solubility limit of the parent matrix then concentration of oxygen vacancies become independent of temperature and oxygen pressure in these systems. The conductivity values for all the samples are calculated and summarized in table 4.16. The data reveal that the conductivity of undoped YNbO_4 is of the order of 10^{-8} Scm^{-1} and YNS-4 sample exhibits the highest conductivity of $1.26 \times 10^{-3} \text{ Scm}^{-1}$. A major conductivity difference observed in YNS-4 sample i.e., $1.26 \times 10^{-3} \text{ Scm}^{-1}$ shows that this sample exhibits higher vacancies which provide path for ion conduction. Similar results have also been observed in case of Y_2O_3 - 20 mol% Nb_2O_5 possessing maximum ionic conductivity due to presence of oxygen vacancies [73].

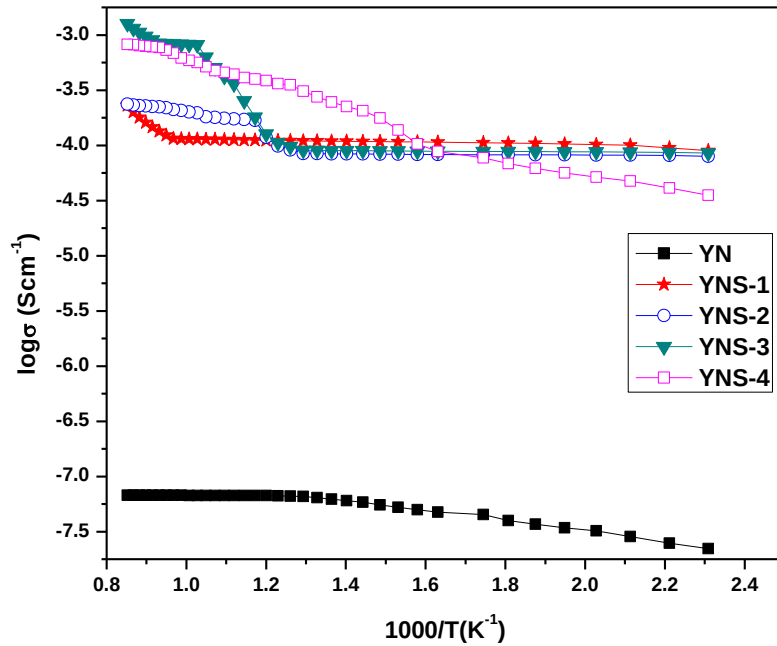


Figure 4.42: Arrhenius plots of YNS, YNS-1, YNS-2, YNS-3 and YNS-4 samples.

The activation energy can be calculated from the slope of arrhenius plot. In present case, the activation energy lies between 0.78-0.20 eV as given in table 4.16. The observed conductivity measurements of various compositions are in good agreement with activation energy trend. Similar observations have also been reported in various $\text{Bi}_4\text{V}_{2-x}\text{Ti}_x\text{O}_{11-\delta}$ ($0 \leq x \leq 0.4$) based systems [48].

Table 4.16: Electrical conductivity, activation energy and thermal expansion coefficient of YNS, YNS-1 to YNS-4 samples respectively.

Sample Name	Conductivity $\sigma_{900^\circ\text{C}}(\text{Scm}^{-1})$	$E_a > 750^\circ\text{C}$ (eV)	TEC ($\times 10^{-6} \text{ K}^{-1}$)
YNS	6.77×10^{-8}	1.03	8.47
YNS-1	3.0×10^{-4}	0.89	8.37
YNS-2	2.36×10^{-4}	0.79	8.3
YNS-3	8.23×10^{-4}	0.76	8.32
YNS-4	1.26×10^{-3}	0.68	8.39

4.4 Sr^{2+} and Ca^{2+} doped $\text{La}_2\text{Ti}_2\text{O}_7$ layered perovskite systems

In this series, the effect of systematic doping of SrO and CaO for La_2O_3 in $\text{La}_2\text{Ti}_2\text{O}_7$ system was investigated. Different concentration of Sr^{2+} and Ca^{2+} doping was chosen to find the relationship between conductivity, thermal and structural properties of Sr and Ca doped $\text{La}_2\text{Ti}_2\text{O}_7$ system. The

as prepared samples were characterized by different techniques to check their above mentioned properties. The obtained results and their analysis are given in the following section.

4.4.1 Density analysis

The resulting samples show good sinterability at 1300 °C and density obtained is nearly 90% of the theoretical density for undoped LST sample [74]. LST-1, LST-2, LST-3 and LST-4 samples exhibits lower densities than undoped LST sample as indicated in table 4.17, respectively. The decrease in density of LST-1, LST-2, LST-3, LST-4 samples seems to be related with the formation of minor phase whose volume fraction increases with increase in concentration of Sr^{2+} dopant. Since, density is the additive property. So, higher atomic mass element is replaced by lower atomic mass element leading to decrease in density. In the present system, the atomic mass of solute (Sr/Ca) is less than the solvent La. Moreover, the formation of secondary phase, in general, segregates along the grain boundary which prevents proper grain growth of the major phase. This segregation leads to higher disorderness in microstructure and results in decrease in the density of the system. On the other hand, no significant change in density is observed for LCT-1, LCT-2, LCT-3 and LCT-4 samples.

Table 4.17: Relative densities of LST-1 to LST-4, LCT-1 to LCT-4 samples, respectively.

Sample Name	LST	LST-1	LST-2	LST-3	LST-4	LCT-1	LCT-2	LCT-3	LCT-4
Relative Density (%)	90	82.5	80	78	76.5	86	85	85	86

4.4.2 X-ray diffraction analysis (XRD)

XRD of LST, LST-1, LST-2, LST-3, LST-4, LCT-1, LCT-2, LCT-3 and LCT-4 samples are shown in the figure 4.43 (a) and 4.43 (b). X-ray diffraction pattern of LST samples shows the formation of $\text{La}_2\text{Ti}_2\text{O}_7$ (ICDD Card No. = 01-081-1066). Similar results have also been reported

for layered perovskite systems [74]. All the XRD peaks are indexed with monoclinic layered perovskite phase. However, in comparison to LST sample, LST-1, LST-2, LST-3, LST-4 samples exhibit additional secondary phase of $(\text{Sr}_{2.85}\text{La}_{0.15})(\text{Ti}_2\text{O}_{6.875})$ (ICDD Card No. = 01-089-0090). The above result is in good agreement with the result obtained by Takamura et al., [74] where $\text{La}_2\text{Ti}_2\text{O}_7$ and secondary phase of $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$ was obtained for Sr doped $\text{La}_2\text{Ti}_2\text{O}_7$ sample at 1300 °C. On the other hand, the higher concentration of doping ($x = 0.1, 0.2, 0.3$ and 0.4) disrupt the $\text{La}_2\text{Ti}_2\text{O}_7$ phase and leads to formation of $(\text{La}_{0.4}\text{Ca}_{0.6})(\text{TiO}_3)$ (ICDD card No. = 01-072-6409) minor phase in case of LCT-1, LCT-2, LCT-3, LCT-4 samples. In other words, as soon as Sr^{2+} and Ca^{2+} increases above critical value, it induces the phase separation and form $(\text{Sr}_{2.85}\text{La}_{0.15})(\text{Ti}_2\text{O}_{6.875})$ phase as well as $(\text{La}_{0.4}\text{Ca}_{0.6})(\text{TiO}_3)$ phase in $(\text{La}_{1-x}\text{Sr}_x\text{TiO}_y)$ and $(\text{La}_{1-x}\text{Ca}_x\text{TiO}_y)$ where ($x=0.1, 0.2, 0.3$ and 0.4) respectively. The substitution of La^{3+} with cation of lower valence state (Sr^{2+}) causes an electronic unbalance in the layered perovskite lattice that can be compensated either with the generation of oxygen vacancy or change in B cationic site at higher oxidation state. The lattice parameter calculated for LST ($x=0$) sample shows slight increase e.g., $a=7.83\text{\AA}$, $b=5.56\text{\AA}$ and $c=13.02\text{\AA}$. In general, higher ionic radii doping increases the lattice parameter which is in agreement with the present results [17, 22, 23]. Many reports have appeared in the literature relating to lattice parameters and their variation with dopants. Moreover, it is observed that when the secondary crystalline phases are formed, then the lattice parameters of the first phase becomes invariable and independent to the dopants [75-77].

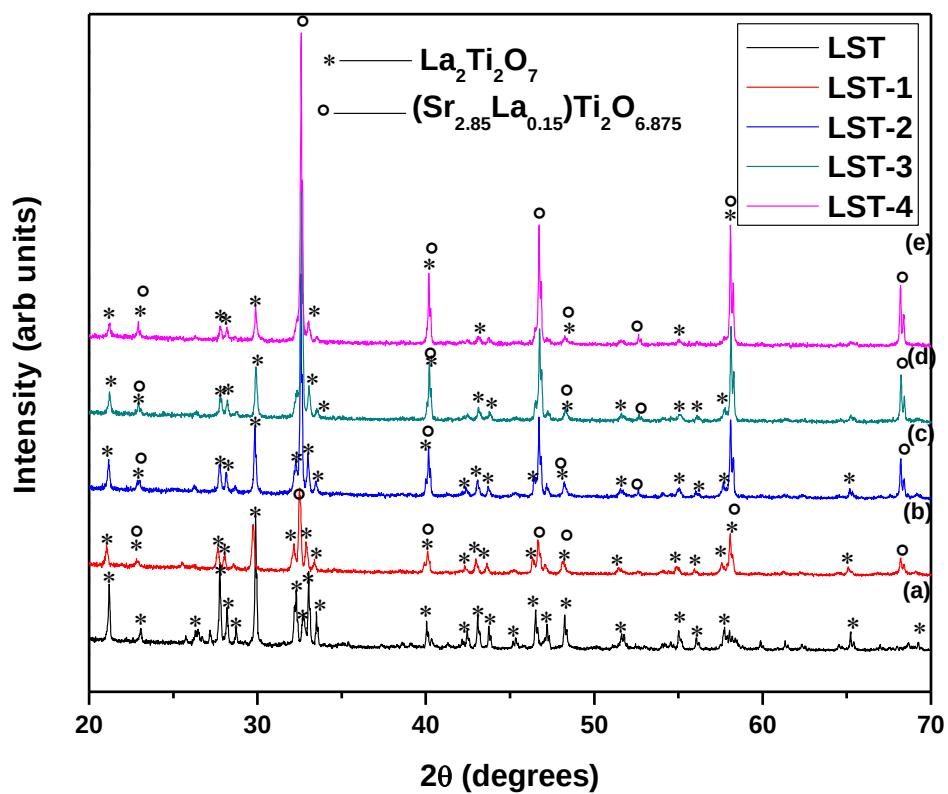


Figure 4.43 (a): X-ray diffraction pattern of (a) LST, (b) LST-1, (c) LST-2, (d) LST-3 and (e) LST-4 samples.

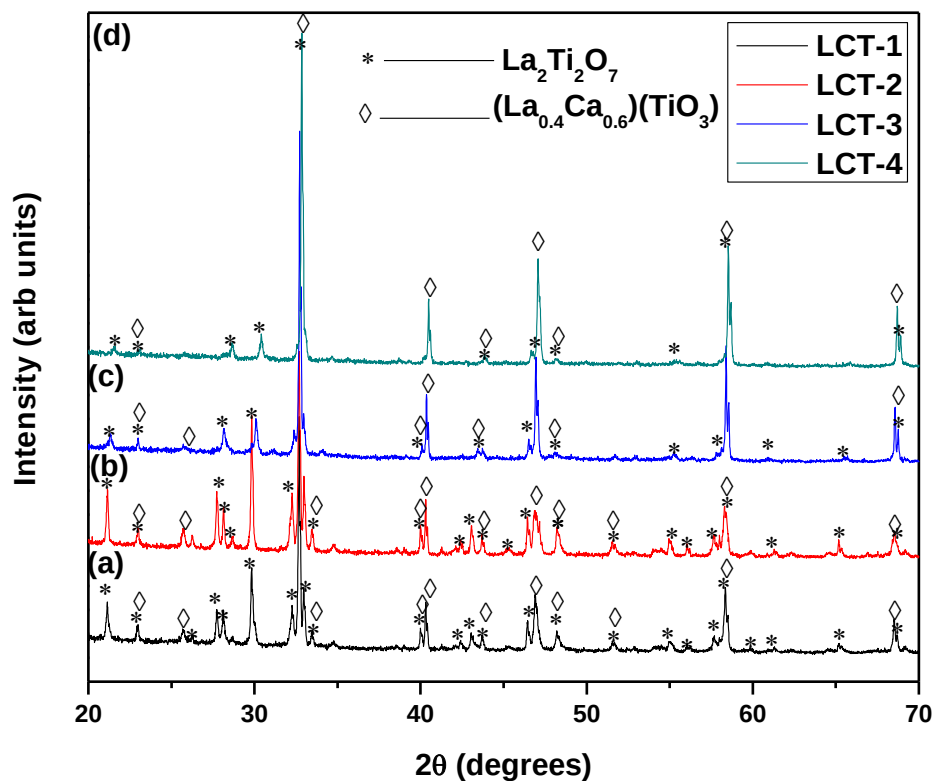


Figure 4.43 (b): X-ray diffraction pattern of (a) LCT-1, (b) LCT-2, (c) LCT-3 and (d) LCT-4 samples.

4.4.3 FT-IR analysis

FT-IR spectra of LST, LST-1, LST-2, LST-3 and LST-4 samples are shown in figure 4.44 (a) and LCT-1, LCT-2, LCT-3, LCT-4 samples are shown in figure 4.44 (b). Similar FT-IR spectra except some change in band intensity and position for all samples was observed. The absorption bands at 640 cm^{-1} , 850 cm^{-1} are observed for La_2O_3 in both figures [58]. Moreover, anatase and rutile phases of titania exhibits strong absorption bands in the region of $650\text{--}850\text{ cm}^{-1}$ [77]. In addition to this, the appearance of absorption bands whose intensity increases with increase in Ca^{2+} content around 2400 cm^{-1} in LCT-1, LCT-2, LCT-3, LCT-4 samples can be attributed to the presence of Ca-O band in figure 4.44 (b). Moreover, bands of lesser intensity around 1450 cm^{-1}

and 3600 cm^{-1} which are mainly due to CaO are observed [78]. Broadening between 600 cm^{-1} and 900 cm^{-1} band, after doping of Sr^{2+} in LST, LST-1, LST-2, LST-3, LST-4 samples is a clear manifestation of weakening of La-O bond. It may be associated with formation of mixed bond of La-O and Sr-O in these samples. In other words, FT-IR spectra shows monoclinic phase with layered perovskite structure of $\text{La}_2\text{Ti}_2\text{O}_7$ that has formed in all the samples. The host matrix of $\text{La}_2\text{Ti}_2\text{O}_7$ becomes weak with addition of Sr^{2+} and Ca^{2+} content in LST to LST-4 samples and LCT-1 to LCT-4 samples, respectively. The broadness in FT-IR spectra is more prominent in Sr^{2+} doped samples as compared to the Ca^{2+} doped $\text{La}_2\text{Ti}_2\text{O}_7$ samples.

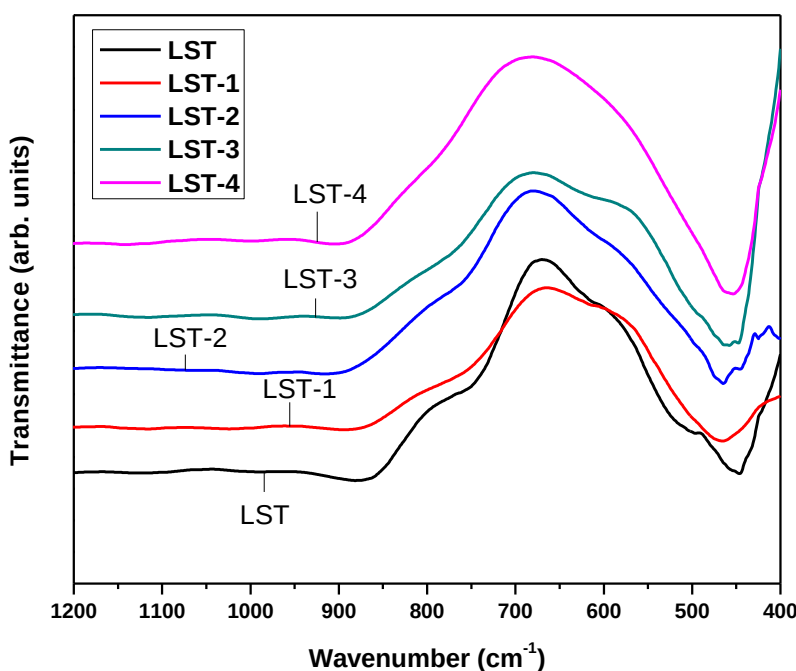


Figure 4.44 (a): FT-IR spectra of LST, LST-1, LST-2, LST-3 and LST-4 samples.

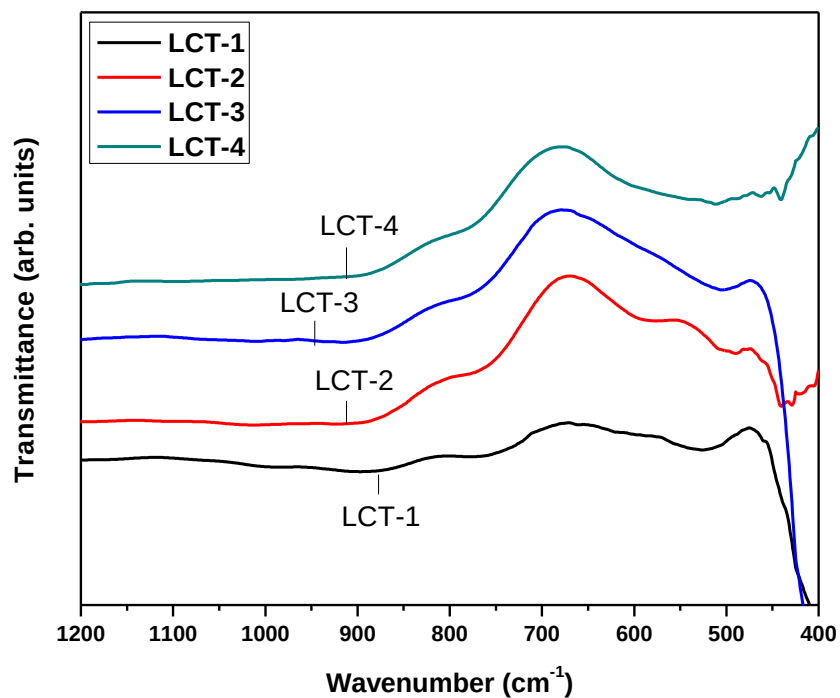


Figure 4.44 (b): FT-IR spectra of LCT-1, LCT-2, LCT-3 and LCT-4 samples.

4.4.4 SEM analysis

The SEM micrographs of fractured surfaces of undoped LST, LST-3, LST-4, LCT-3 and LCT-4 samples are shown in figure 4.45, respectively. The grains are smoothly interconnected with almost zero porosity and appear to possess single phase [79]. On the other hand, doped samples are porous and pores are continual as well as open. The increase in porosity of Sr doped samples results in decrease in relative density as compared to Ca doped samples as indicated in table 4.17. In other words, with increase of volume fraction of minor phase of $(\text{Sr}_{0.1}\text{La}_{0.6})(\text{TiO}_3)$ as shown in XRD of LST-1, LST-2, LST-3, LST-4 samples, impedes the mass transportation and the sintering process leading to decrease in densities of these samples [23]. However, the sintered samples (LCT-1, LCT-2, LCT-3, LCT-4) when analyzed in fractured mode exhibit cracks which result in decrease in relative densities of these samples.

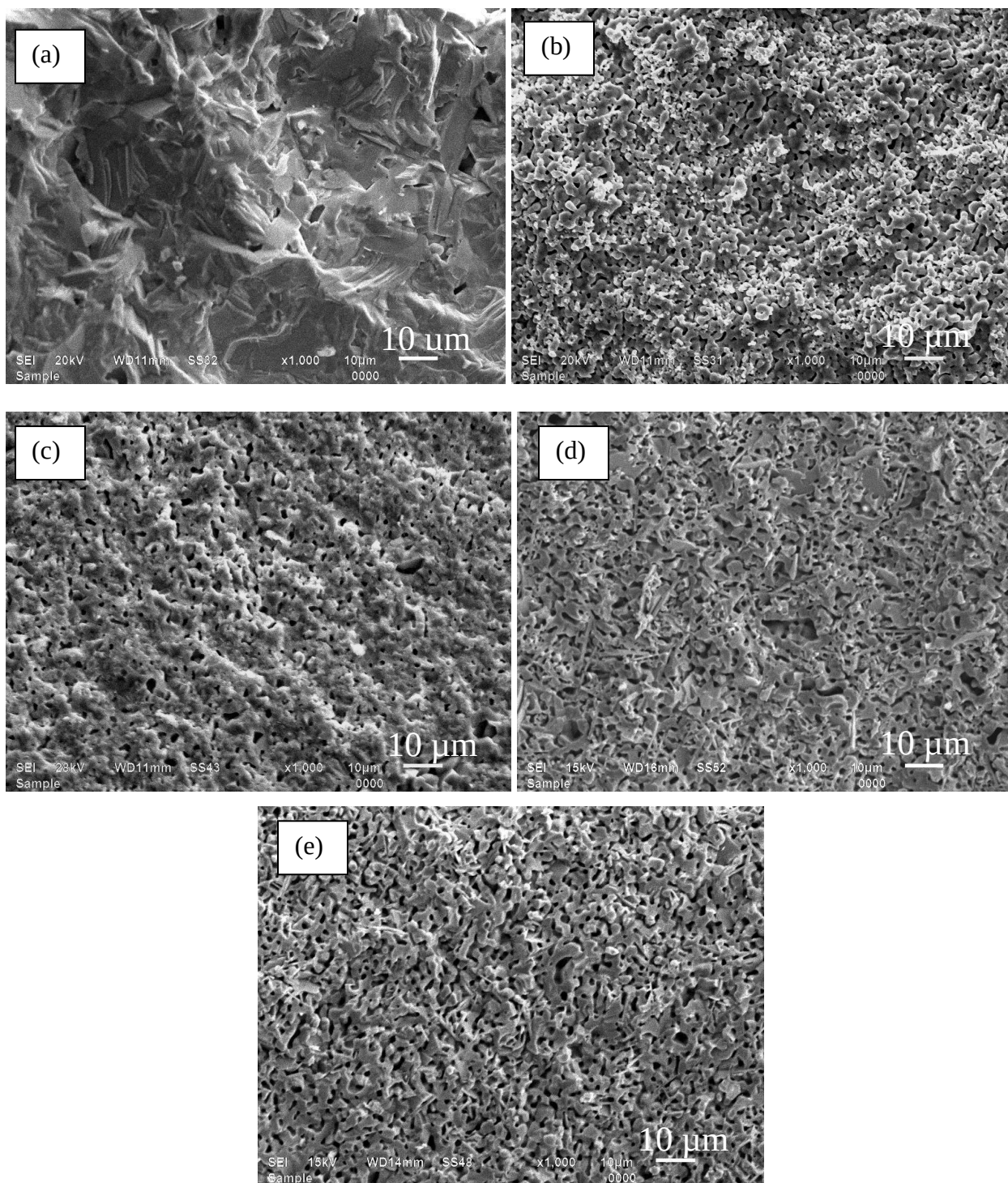


Figure 4.45: SEM of (a) undoped LST (b) LST-3, (c) LST-4, (d) LCT-3, (e) LCT-4, respectively.

4.4.5 Thermal analysis

Thermal gravimetric analysis of LST, LST-1, LST-2, LST-3, LST-4, LCT-1, LCT-2, LCT-3 and LCT-4 samples done in nitrogen atmosphere is shown in figure 4.46 (a) and figure 4.46 (b). The plateau observed in TGA of all the samples at 780°C can be related to the monoclinic to orthorhombic phase transition [78, 80, 81]. However, these transitions diminish for Sr and Ca doped samples. In addition to this, plateau observed in all the samples at ~377°C can be attributed to the electrostatic effect between the oxygen octahedron and the Ti ion resulting in the distortion of the perovskite cell [80]. It is observed that undoped LST sample shows weight gain of 0.25%, LST-1 sample of 0.325%, LST-2, LST-3 and LST-4 sample of nearly 0.175%, LCT-1 sample of 0.075%, LCT-2 sample of 0.275%, LCT-3 and LCT-4 sample of 0.45% in nitrogen atmosphere. This can be due to the presence of oxygen vacancies in the sample [75]. Moreover, samples that exhibit no significant weight change signify greater thermal stability in these samples in nitrogen atmosphere.

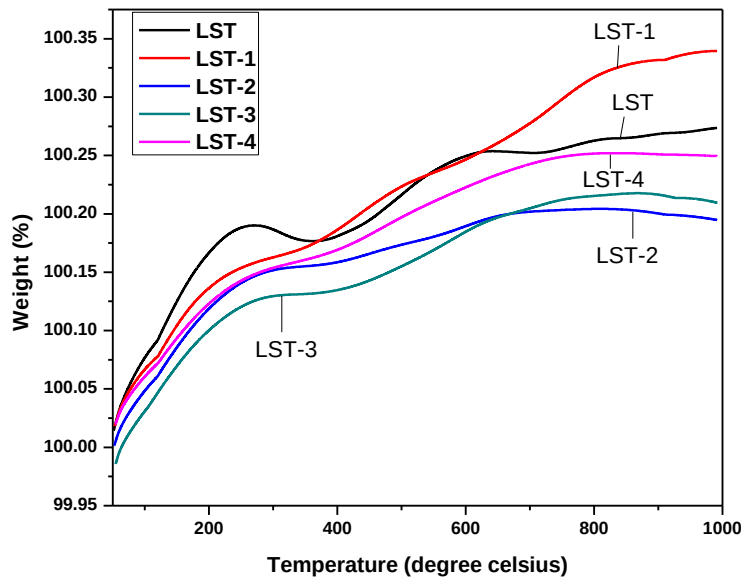


Figure 4.46 (a): Thermo gravimetric analysis of LST, LST-1, LST-2, LST-3 and LST-4 samples in nitrogen atmosphere.

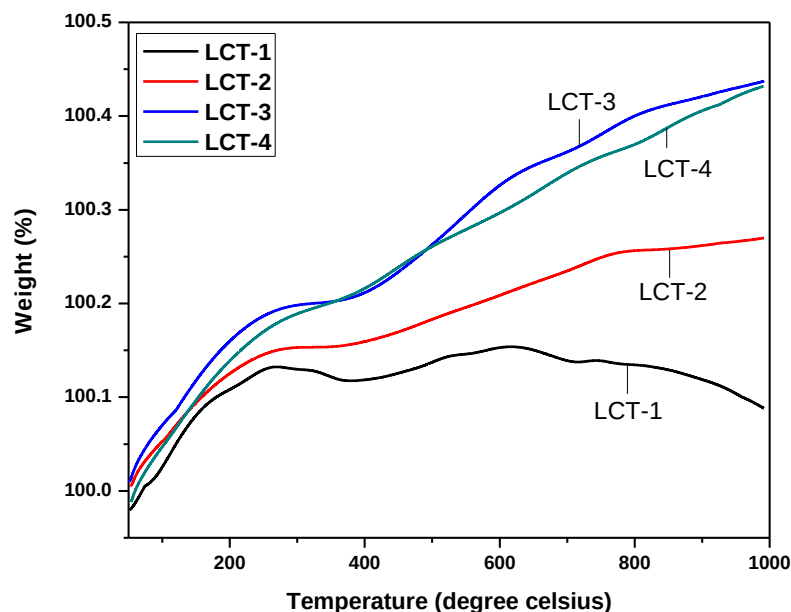


Figure 4.46 (b): Thermo gravimetric analysis of LCT-1, LCT-2, LCT-3 and LCT-4 samples in nitrogen atmosphere.

4.4.6 Electrical conductivity measurement

The $\log \sigma$ versus $1000/T$ plots for all samples are shown in figure 4.47 (a) and 4.47 (b), respectively. The conducting behavior of LST, LST-1, LST-2, LST-3 and LST-4 samples shows linear behavior up to 900°C. In addition to these, minor fluctuations are observed in all the samples. These minor fluctuations can be due to presence of mixed behavior of ions and electrons. Moreover, phase transitions from monoclinic to orthorhombic phase is observed at high temperatures which are clearly visible in LCT-1 to LCT-4 samples (figure 4.47 (b)). However, Takamura et al., [74] measured the conductivity of undoped $\text{La}_2\text{Ti}_2\text{O}_7$ and Sr doped $\text{La}_2\text{Ti}_2\text{O}_7$ and found that compounds in the La-Ti system are considered to be oxygen ion conductors due to the presence of Frenkel defects. Moreover, the ionic conductivity of $(\text{La}_{0.9}\text{Sr}_{0.1})_2\text{Ti}_2\text{O}_7$ was found to be less than the undoped sample. Similar behavior was observed

in the present samples. The decrease in ionic conductivity can be attributed to the lesser number of shear planes in Sr doped $\text{La}_2\text{Ti}_2\text{O}_7$ in comparison to undoped $\text{La}_2\text{Ti}_2\text{O}_7$. In other words, layered perovskite structure consists of perovskite-type slabs and the shear planes between these slabs contain oxygen layer which is a major source of Frenkel defects [76]. The higher number of planes has higher number of oxygen layers. These layers exhibit oxygen vacancies which are responsible for higher oxide ion conductivity. The conductivity values for all the samples are calculated and summarized in table 4.18.

Table 4.18: Electrical conductivity, activation energy and thermal expansion coefficient of LST, LST-1 to LST-4, LCT-1 to LCT-4 samples, respectively.

Sample Name	Conductivity $\sigma_{900^\circ\text{C}} (\text{Scm}^{-1})$	$E_a > 750^\circ\text{C}$ (eV)	TEC ($\times 10^{-6} \text{K}^{-1}$)
LST	2.67×10^{-5}	0.78	8.36
LST-1	2.35×10^{-6}	0.81	8.54
LST-2	2.12×10^{-6}	0.86	8.42
LST-3	1.81×10^{-6}	0.82	8.46
LST-4	1.47×10^{-6}	0.89	8.63
LCT-1	1.33×10^{-5}	0.83	8.53
LCT-2	9.95×10^{-5}	0.80	8.61
LCT-3	7.77×10^{-4}	0.78	8.88
LCT-4	9.46×10^{-4}	0.76	8.68

The data reveal that the conductivity of undoped $\text{La}_2\text{Ti}_2\text{O}_7$ exhibits the highest conductivity of $2.67 \times 10^{-5} \text{Scm}^{-1}$. Whereas, doped samples shows lower conductivity by one order of magnitude for Sr doped samples. This can be attributed to the decrease in the number of shear planes in the

layered structure of perovskite with general formula of $AE_{n-4}La_4Ti_nO_{3n+2}$ (AE=alkaline earth metal) with $n=4.5$ [76]. On the other hand, the conductivity of Ca-doped $La_2Ti_2O_7$ has been found to be of p-type under oxidizing conditions [82]. It is observed that value of conductivity increases by one order with increase in concentration of Ca content in LCT-3 and LCT4 samples, respectively. The activation energy can be calculated from the slope of arrhenius plot. In present case, the activation energy lies between 0.76-0.83 eV as given in table 4.18, respectively. The observed conductivity measurements of various compositions are in good agreement with activation energy trend [82]. The values of activation energy clearly indicate that the present systems are predominantly ionic conductors either of the category of oxide ion conductors or protonic ion conductors.

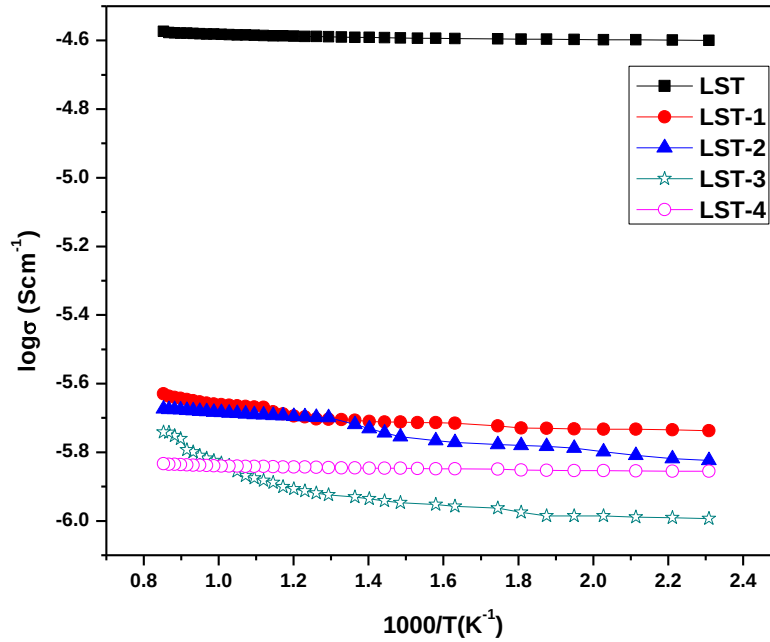


Figure 4.47 (a): Arrhenius plots of LST, LST-1, LST-2, LST-3 and LST-4 samples.

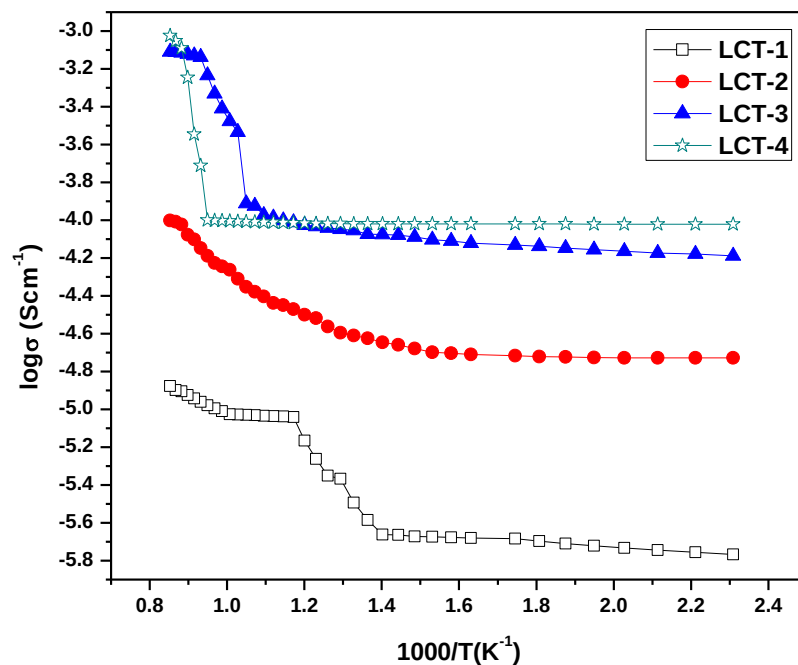


Figure 4.47 (b): Arrhenius plots of LCT-1, LCT-2, LCT-3 and LCT-4 samples.

4.5 Chemical interaction between 40SiO₂.30BaO.20ZnO.10Y₂O₃ glass and Ca²⁺ doped yttrium titanate electrolyte

In this section, the chemical interaction study between candidate glass sealant (40SiO₂.30BaO.20ZnO.10Y₂O₃) and Ca²⁺ doped Y₂Ti₂O₇ system is given. The selection of Ca²⁺ doped pyrochlore is based on its better thermal stability and presence of Y₂O₃ in both samples of glass sealant and electrolyte. The purpose of this study was to understand the kinetics of the formation of different crystalline phases with respect to the heat treatment temperature and duration. The results are discussed in the light of various crystalline phase formations, their volume fractions and its effect on various properties. It was observed that after heat treatment of all the samples Y₂Ti₂O₇, BaZn(SiO₄) and Ca(SiO₃) phases have formed. In addition to this,

detrimental phase (in case of SOFCs application) of SiO_2 is also observed in all the samples. The qualitative volume fraction of formed phases depends upon the duration of heat treatment.

4.5.1 X-ray diffraction analysis (XRD)

The XRD of all the samples INY-1, INY-2, INY-3 and INY-4 are shown in the figure 4.48. The phases formed in all the samples are $\text{Y}_2\text{Ti}_2\text{O}_7$ (ICDD Card No. = 01-087-1849), $\text{BaZn}(\text{SiO}_4)$ (ICDD Card No. = 01-081-2318), $\text{Ca}(\text{SiO}_3)$ (ICDD Card No. = 01-088-1922) and SiO_2 (ICDD Card No. = 01-082-1405). The volume fraction of crystalline phases is depicted in figure 4.49. It is observed that the volume fraction of $\text{Y}_2\text{Ti}_2\text{O}_7$ and $\text{BaZn}(\text{SiO}_4)$ phase increases with increasing heat treatment duration. The volume fraction of $\text{Y}_2\text{Ti}_2\text{O}_7$ phase increases due to diffusion of Y from the glass matrix since glass structure is open structure [83]. On the other hand, CaSiO_3 is formed which is considered to be the most common product in most of the powder mixtures during chemical interaction study [83]. It is well known fact, that solute atom whether it is substitution solution or interstitial solution comes out from the base matrix easily as compared to the host matrix. Obviously in the present case, the Ca^{2+} might segregate first and interact with the glass sealant from the CaSiO_3 phase. In addition to this, detrimental phase of cristobalite (SiO_2) is also formed during chemical interaction but it is interesting to note that the volume fraction of SiO_2 phase decreases with increase in heat treatment duration. However, it is not desirable phase for SOFC application. The observed results between glass and doped electrolyte is in well agreement with the results reported by Bahadur et al. [84] and N. Lahl et al., [85]. The formation of the crystalline phases during heat treatment is governed by the chemical nature of oxides as well as cations within the glass and doped electrolyte [86]. Conclusively, the diffusion of Ca^{2+} from pyrochlore ($\text{Y}_{1.8}\text{Ca}_{0.2}\text{Ti}_2\text{O}_7$) and Y^{3+} from glass has taken place resulting in change in volume fraction of the different crystalline phases.

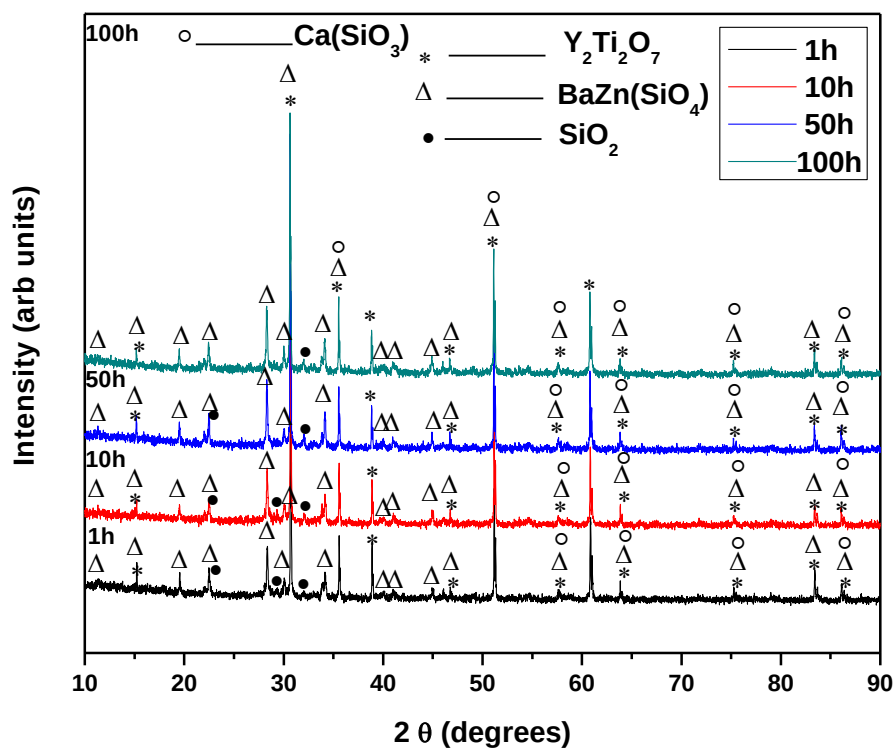


Figure 4.48: X-ray diffraction pattern of (a) INY-1, (b) INY-2, (c) INY-3 and (d) INY-4 samples respectively.

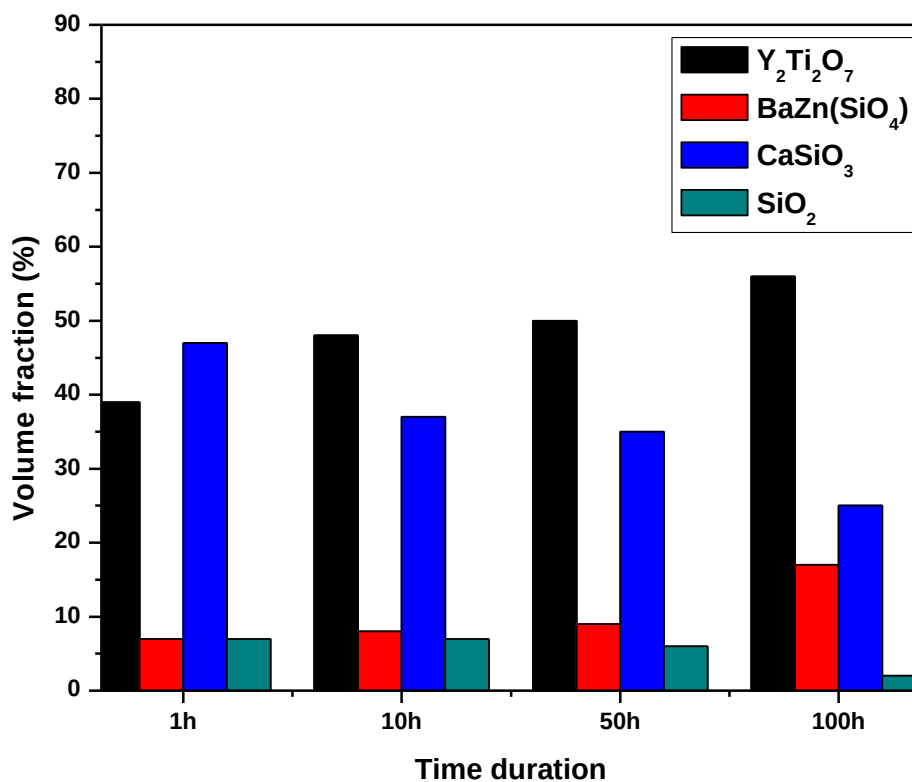


Figure 4.49: Volume fraction of crystalline phases formed during heat treatment of all the samples.

4.5.2 SEM and EDS analysis

The SEM micrographs of fractured surfaces of INY-1, INY-2, INY-3 and INY-4 samples are shown in figure 4.50, respectively. These images provide the information regarding grain size, shape, porosity and agglomeration of the powder. The distribution of the grains are non-uniform in all the samples. It is observed that all the samples are porous and pores are continual as well as open. Moreover, some of the grains exhibit faceted morphology. In addition to this, river flow pattern is also observed at the fractured area of the grains of INY-1 sample (figure 4.50 (a)) which is typical characteristic of brittle structure. Though this variation is not much but observable. These features are also observed for INY-2 to INY-4 samples where $CaSiO_3$ phase

tries to fill the pore as can be seen from the flow pattern. In contrast to this, $(Y_{1-x}Ca_x)_2Ti_2O_{7-x}$ for $x=0.1$ consists of grains with closed pores and river flow pattern is observed on certain grains. The EDS analysis was done on surfaces of INY-1, INY-2, INY-3 and INY-4 samples. It clearly indicates the presence of $Y_2Ti_2O_7$ and $BaZn(SiO_4)$ phases whose volume fraction is large in comparison to other phases. The elemental analysis of INY-1, INY-2, INY-3 and INY-4 samples (as indicated in table 4.19) indicate that all the samples are rich in $Y_2Ti_2O_7$ as well as $BaZn(SiO_4)$ phase. Clearly, the weight % of yttria goes on increasing and weight % of Si goes on decreasing from INY-1 to INY-4 samples. The overall analysis indicates that volume fraction of $Y_2Ti_2O_7$ phase increases with increase in heating duration time. The EDS analysis clearly depicts the atomic percentage of various elements to be in agreement with the volume fraction obtained from XRD analysis.

Table 4.19: EDS analysis of various elements in the INY-1, INY-2, INY-3 and INY-4 samples.

Element	Atomic %			
	INY-1	INY-2	INY-3	INY-4
O	92.46	91.22	91.53	92.15
Si	2.90	2.58	2.87	2.56
Ti	0.75	1.15	0.78	0.71
Zn	0.02	0.11	0.14	0.05
Y	3.91	4.42	4.28	4.27
Ba	0.23	0.52	0.40	0.26

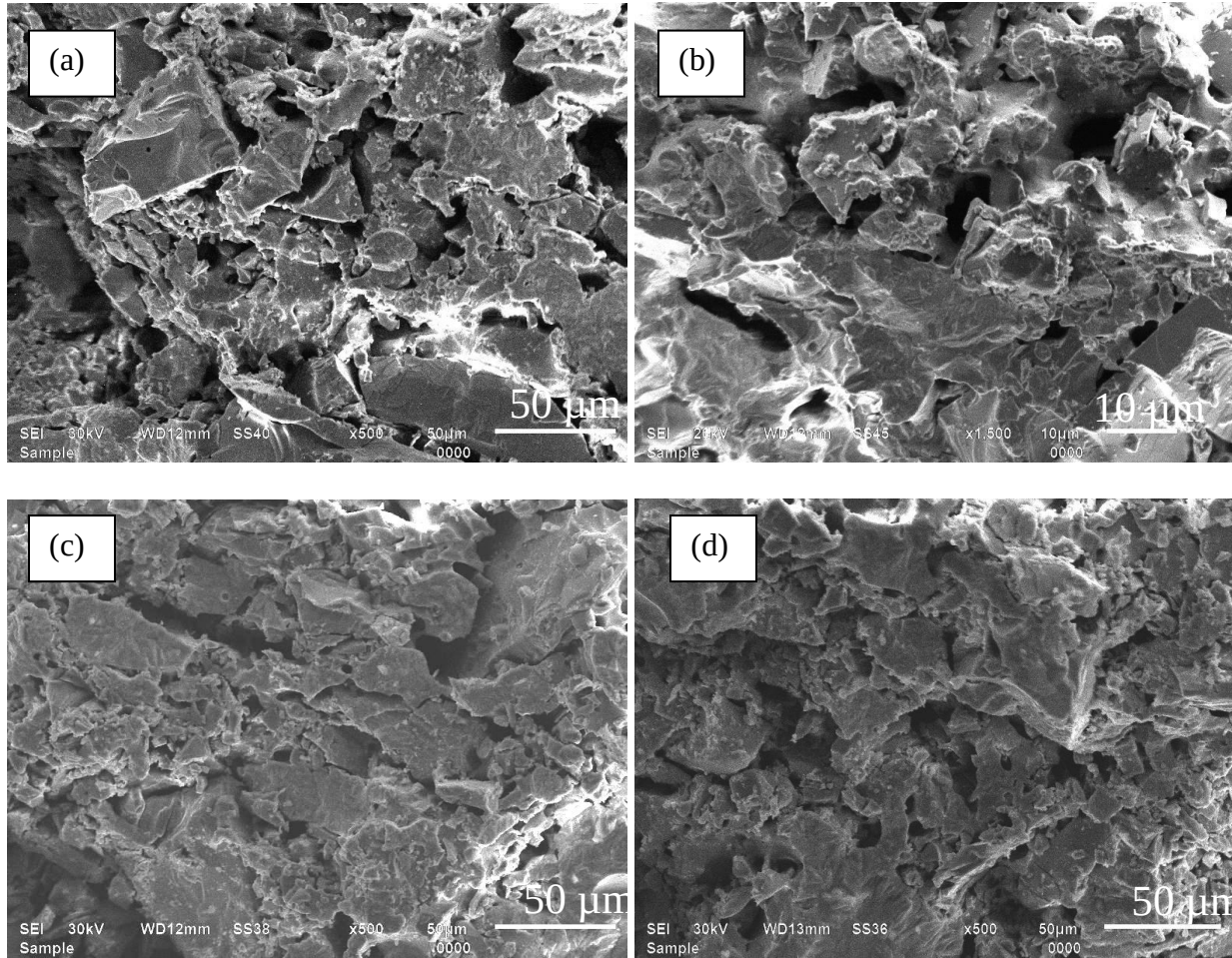


Figure 4.50: SEM micrographs of (a) INY-1, (b) INY-2, (c) INY-3 and (d) INY-4 samples at various magnifications.

4.5.3 Thermal expansion coefficient (TEC)

Table 4.20 shows the TEC values of INY-1, INY-2, INY-3 and INY-4 samples. The thermal expansion coefficient of the glass and the electrolytes are $8.5 \times 10^{-6} \text{ K}^{-1}$ and $8.4 \times 10^{-6} \text{ K}^{-1}$ respectively. The TEC value of INY-1, INY-2, INY-3 and INY-4 samples is found to be very close to reported value of TEC of other components of SOFCs [87]. It is observed that thermal expansion coefficient of samples increases with heat treatment duration time. This type of trend

in TEC might have arisen due to the presence of cristobalite (SiO_2) phase in all the samples. As heat treatment duration increases the volume fraction of SiO_2 phase decreases.

Table 4.20: Thermal expansion coefficient of INY-1, INY-2, INY-3 and INY-4 samples respectively.

Sample name	TEC ($\times 10^{-6} \text{ K}^{-1}$)
INY-1	8.24
INY-2	8.25
INY-3	8.32
INY-4	8.64

Contrary to this, the volume fraction of $\text{BaZn}(\text{SiO}_4)$ and CaSiO_3 phases increases with respect to heat treatment duration. This variation has caused increasing trend in TEC in present sample. It is found that the volume fraction of detrimental phase of SiO_2 decreases with increase in heat treatment time of INY-1, INY-2, INY-3 and INY-4 samples.

4.5.4 Electrical conductivity measurement

The real and imaginary part of impedance are plotted with change in frequency at various temperatures i.e., 400 °C, 600 °C, 800 °C and 900 °C respectively for INY-4 sample as indicated in figure 4.51. The selection of INY-4 sample is done because the thermal expansion coefficient of this sample is higher than other samples and close to the required TEC for SOFCs applications. The $\log \sigma$ versus $1000/T$ plots for INY-4 sample is shown in figure 4.52. The conducting behavior of INY-4 sample shows linear behavior up to 400 °C. Below 900°C, at 500°C and 700°C arrhenius plot of INY-4 sample shows some fluctuations. These fluctuations can be attributed to the presence of $\text{Y}_2\text{Ti}_2\text{O}_7$ phase in the system which shows extrinsic to intrinsic transitions at 500 °C and order to disorder transitions at 700 °C. The conductivity of

INY-4 sample comes out to be $8.63 \times 10^{-8} \text{ Scm}^{-1}$ at 900°C with activation energy of 0.8 eV. In contrast to this, the conductivity of $(\text{Y}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_{7-x}$ for $x=0.1$ sample at 900°C was found to be $3.16 \times 10^{-6} \text{ Scm}^{-1}$. The decrease in conductivity can be due to presence of cristobalite phase in the system as indicated from XRD shown in figure 4.48. The cristobalite are insulator [88]. The overall conductivity of the system, in general, follows the mixture rule.

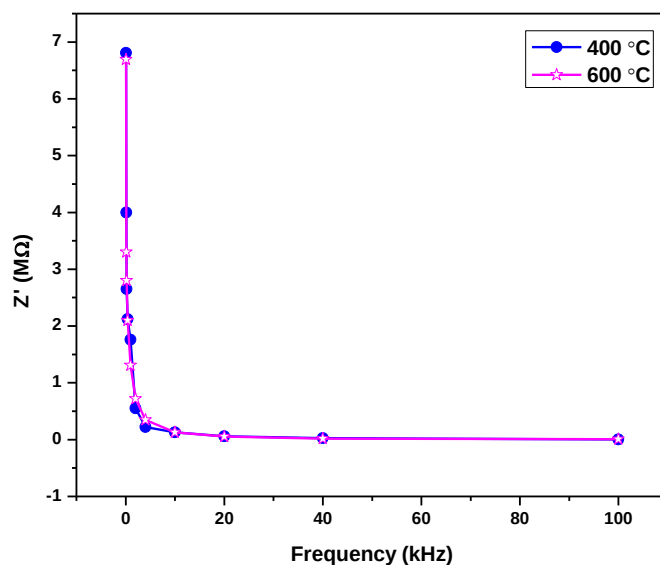


Figure 4.51 (a): Variation of real part of complex impedance (Z') of INY-4 sample at 400°C and 600°C .

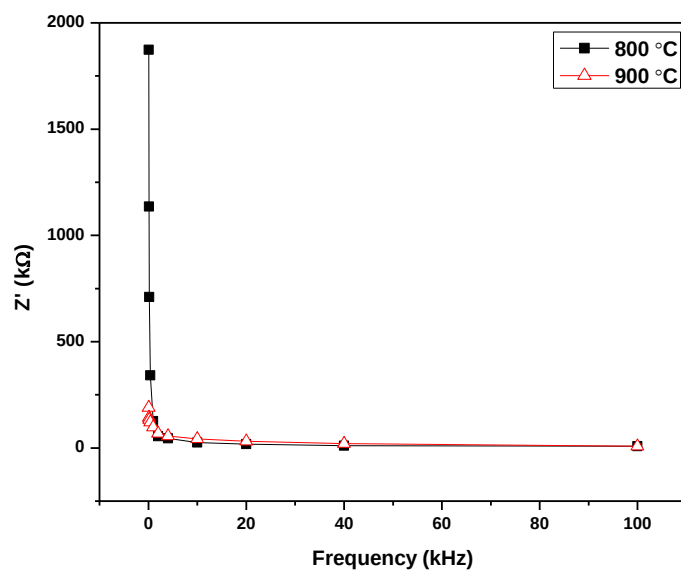


Figure 4.51 (b): Variation of real part of complex impedance (Z') of INY-4 sample at 800 °C and 900 °C.

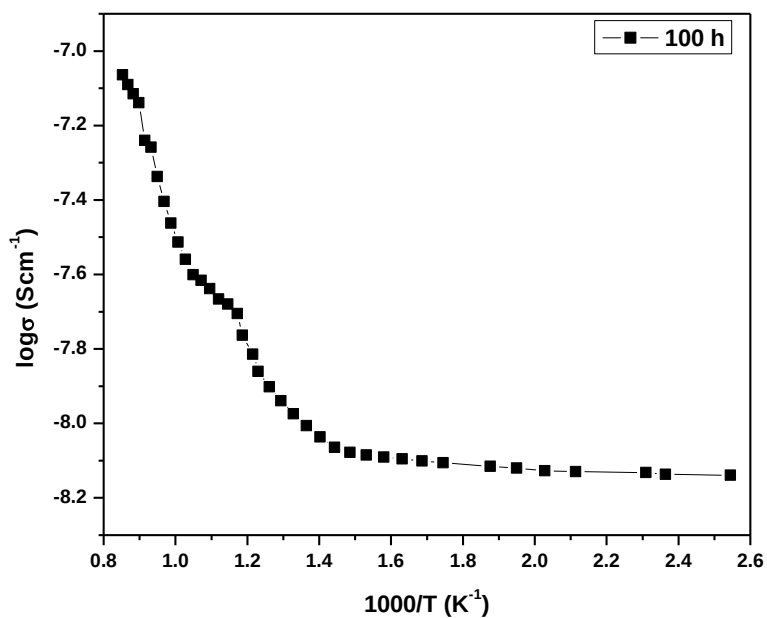


Figure 4.52: Arrhenius plot of INY-4 sample.

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CONCLUSIONS AND SCOPE OF THE FUTURE WORK

5.1 Conclusions

Pyrochlore structured materials can be used as solid electrolyte in solid oxide fuel cell. Since, the performance of solid oxide fuel cell depends primarily on ionic conductivity of electrolyte so, the study of $\text{Y}_2\text{Ti}_2\text{O}_7$ pyrochlore based system was undertaken in the present work to establish their potential applications as electrolyte material for solid oxide fuel cell. The change in processing condition leads to the formation of two different phases, i.e., perovskite and pyrochlore even taking same initial ingredients with same concentration. The formation of YTlO_3 phase is due to the reduction of Ti^{4+} to Ti^{3+} at fast heating rate. On the other hand, pyrochlore phase is formed when heating rate is slow with intermediate holdings. The growth of YTlO_3 phase is an interface dependant feature which has occurred due to prevailing reducing (oxygen deficient) atmosphere inside the furnace.

The doping of Sr^{2+} and Ca^{2+} in $\text{Y}_2\text{Ti}_2\text{O}_7$ system leads to different phase formation and solid solubility. Sr^{2+} doping up to $x = 0.1$ results in the formation of the solid solution and enhances the structural ordering which is responsible for slight decrease in ionic conductivity. Further doping of Sr^{2+} in the present system leads to growth of SrTiO_3 secondary phase. The conductivity in monophasic samples depends upon the oxygen vacancies which were created by the dopant to maintain the charge neutrality. Among all the samples, $\text{Y}_{1-x}\text{Sr}_x\text{TiO}_y$ with $x=0.4$ i.e., YST-4 sample shows the maximum conductivity i.e., $1.50 \times 10^{-1} \text{ S cm}^{-1}$ at 900°C due to electronic conductivity contribution as indicated by band gap measurement. Similarly, the higher doping of Ca results in the formation of the secondary phase (CaTiO_3) with increase in porosity and decrease in relative densities. The entire samples exhibit the conductivity order of $10^{-7} \text{ S cm}^{-1}$

¹ at higher temperature. FT-IR results show the presence of Ti-O and Y-O bending and stretching vibrations. It was found that with increase in dopant concentration these bands become more diffused indicating higher disordering in the samples. The values of activation energies obtained in the present study clearly indicate that most of the samples are ionic conductors. In addition to this, the samples are also found to follow the linear behavior of Arrhenius plots which are another manifestation of the ionic conductivity contribution in the system. The thermal expansion coefficient of the various samples was found in the range of $8 \times 10^{-6} \text{ K}^{-1}$ which is very much in the required range of the SOFCs applications.

It is observed that the doping of Sr^{2+} and Ca^{2+} plays very crucial role to increase the disordering as well oxygen vacancies leading to increase in conductivity values of $\text{Y}_2\text{Ti}_2\text{O}_7$ system. On the other hand, it is found that higher doping concentration leads to secondary phase formation which inhibits the grain growth that ultimately reduces density with increase in porosity. Moreover, it is observed that effect of Ca^{2+} doping in $\text{Y}_2\text{Ti}_2\text{O}_7$ system is more effective than Sr^{2+} doping in $\text{Y}_2\text{Ti}_2\text{O}_7$ system due to occurrence of higher disordering leading to decrease in density with increase in porosity.

When doped with Sr^{2+} , the physical appearance of doped LaNbO_4 is varied with the dopant concentration. The change in color of the samples occurred due to change in the volume fraction of the phases as well as change in transition state of the transition metals. In contrast to this, no significant change in color is observed in the Ca^{2+} doped LaNbO_4 samples. The XRD patterns of doped samples indicate the formation of secondary phase with its increasing volume fraction. The FT-IR results of doped samples show the weakening of La-O bond in matrix of LaNbO_4 . It is observed that $\text{La}_{0.95}\text{Sr}_{0.05}\text{NbO}_4$ phase is more conducting than LaNbO_4 phase. A major conductivity difference observed in LNS-4 sample i.e., $1.01 \times 10^{-1} \text{ Scm}^{-1}$ shows that this sample

exhibits higher vacancies which provide path for ion conduction. The UV visible results also show the drastic change in band gap of this particular sample ~ 2.6 eV.

In addition to above system, the effect of systematic doping of Sr and Ca for Y_2O_3 in $YNbO_4$ system was also studied. It was observed that the undoped sample exhibit single phase i.e., $YNbO_4$. The doping of Sr^{2+} in present system leads to secondary phase formation such as $Sr_2Nb_2O_7$ and $SrNb_2O_6$. The formed secondary phases enhance the electrical conductivity by five orders of magnitude. A major conductivity difference observed in YNS-4 sample i.e., $1.26 \times 10^{-3} \text{ Scm}^{-1}$ shows that this sample exhibits higher vacancies which provide path for ion conduction. On the other hand, Ca doped samples exhibit the micro cracks. These cracks have arisen due to negative thermal expansion of secondary phase ($CaNb_2O_6$). The FT-IR spectra become broaden after doping due to weakening of Y-O and Nb-O bonds. However, the bands are sharper in Ca-doped sample as compared to Sr doped samples.

The interaction study of these two systems $Y_2Ti_2O_7$ (electrolyte) and $40SiO_2.30BaO.20ZnO.10Y_2O_3$ based glasses have been done for study of chemical interactions between them to understand the kinetics of the formation of different crystalline phases with respect to the heat treatment temperature and duration. Different crystalline phases such as $Y_2Ti_2O_7$, $BaZn(SiO_4)$ and $Ca(SiO_3)$ have formed during chemical interaction between $(Y_{1-x}Ca_x)_2Ti_2O_{7-x}$ for $x=0.1$ and $40SiO_2.30BaO.20ZnO.10Y_2O_3$ glass. In addition to this, detrimental phase (SiO_2) is also observed in all the samples. However, the volume fraction of SiO_2 phase decreases with increase in duration of heat treatment from INY-1 to INY-4 sample. So, INY-4 sample shows higher thermal stability. The conductivity of INY-4 sample comes out to be $8.63 \times 10^{-8} \text{ Scm}^{-1}$ at 900°C with activation energy of 0.8 eV thus offering higher resistance to flow. Moreover, SEM micrograph clearly shows no crack. However, porosity and very large grains in

all the samples are observed. The overall interaction study indicate that the above system may be a good substitute for long hour operation of SOFC as compared to the existing one as there is no crack observed in the system though porosity exists. The TEC values are also of same order as required for SOFC.

5.2 Scope of the future work

After analyzing the data presented in the thesis, the following suggestions are recommended for further investigation:

- (i) The sample preparation plays an important role to improve the ionic conductivity. Therefore reducing atmosphere conditions should be created inside the furnace for conductivity measurement of the samples.
- (ii) XPS of the systems under study can further provide the details of valence state of the transition metal.
- (iii) The performance of the developed electrolytes should be tested in reducing atmosphere.
- (iv) In present study, the doping concentration of the dopants has been fixed to 10%, 20%, 30% and 40%. The step size of the concentration should be reduced inorder to find the exact solubility limit of the dopant in the solid solution.

List of Publications

- 1) Role of sintering temperature on thermal, electrical and structural properties of $\text{Y}_2\text{Ti}_2\text{O}_7$ pyrochlores, **Jasmeet Kaur Gill**, O.P. Pandey and K. Singh, International Journal of Hydrogen Energy **36** (2011) 14943-14947.
- 2) Ionic conductivity, structural and thermal properties of Ca^{2+} doped $\text{Y}_2\text{Ti}_2\text{O}_7$ pyrochlores for SOFC, **Jasmeet Kaur Gill**, O.P. Pandey and K. Singh, International Journal of Hydrogen Energy **37** (2012) 3857-3864.
- 3) Ionic conductivity, structural and thermal properties of pure and Sr^{2+} doped $\text{Y}_2\text{Ti}_2\text{O}_7$ pyrochlores for SOFC, **Jasmeet Kaur Gill**, O.P. Pandey and K. Singh, Solid State Sciences **13** (2011) 1960-1966.
- 4) Influence of processing conditions on the formation of $\text{Y}_2\text{Ti}_2\text{O}_7$ and YTiO_3 phases, **Jasmeet Kaur Gill**, O.P. Pandey and K. Singh, Transactions of Indian Ceramic Society **70(4)** (2011) 109-114.
- 5) Preparation of $\text{Y}_2\text{Ti}_2\text{O}_7$ pyrochlore using high-energy ball milling and their structural, thermal and conducting properties, M. Singh, **Jasmeet Kaur Gill**, S. Kumar and K. Singh, Ionics **18(5)** (2012) 479-486.
- 6) Structural, thermal and electrical properties of Ti^{4+} substituted Bi_2O_3 solid solutions, Gourav Singla, Paramjyot Kumar Jha, **Jasmeet Kaur Gill** and K. Singh, Ceramics International **38(3)** (2012) 2065-2070.
- 7) Structural, thermal, and electrical properties of $(100-x)\text{ZrO}_2$ (x) Bi_2O_3 compound, Paramjyot Kumar Jha, **Jasmeet Kaur Gill**, Gourav Singla, K. Singh and O. P. Pandey, Ionics (2012) doi: 10.1007/s11581-012-0674-3.
- 8) Structural and electrical study of Sr^{2+} and Ca^{2+} doped yttrium orthoniobates, **Jasmeet Kaur Gill**, O.P. Pandey, K. Singh, Journal of Materials Science (under review).
- 9) Structural, thermal and electrical properties of $\text{Sr}^{2+}/\text{Ca}^{2+}$ doped $\text{La}_{1-x}\text{Sr}_x\text{NbO}_4$ ($0 \leq x \leq 0.4$) system, **Jasmeet Kaur Gill**, O.P. Pandey, B. Chudasama, K. Singh, Solid State Sciences (under review).
- 10) $40\text{SiO}_2.30\text{BaO}.20\text{ZnO}.10\text{Y}_2\text{O}_3$ glass and Ca^{2+} doped yttrium titanate electrolyte-Chemical interaction study for Solid Oxide Fuel Cells, **Jasmeet Kaur Gill**, O.P. Pandey, K. Singh, Physics and Chemistry of Glasses- European Journal of Glass Science and Technology PartB (under review).

List of Papers presented in conference (International/National)

- 1) Ionic conductivity, structural and thermal properties of pure and Sr^{2+} doped $\text{La}_2\text{Ti}_2\text{O}_7$ layered perovskite, **Jasmeet Kaur Gill**, O.P. Pandey and K. Singh, 23rd Annual General Meeting, Functional Materials for sustainable Energy and Advanced Technologies, February 13-15, 2012, Patiala.
- 2) Structural variation in doped and undoped $\text{Y}_2\text{Ti}_2\text{O}_7$ pyrochlores, **Jasmeet Kaur Gill**, O.P. Pandey and K. Singh, 22nd Annual General Meeting, Materials Research Society of India (MRSI), MRSI-AGM-2011, Bhopal.
- 3) Ionic conductivity, structural and thermal properties of Ca^{2+} doped $\text{Y}_2\text{Ti}_2\text{O}_7$ pyrochlores for SOFC, **Jasmeet Kaur Gill**, O.P. Pandey and K. Singh, International Conference on Renewable Energy (ICRE), January 17 – 21 (2011).
- 4) Role of sintering temperature on thermal, electrical and structural properties of $\text{Y}_2\text{Ti}_2\text{O}_7$ pyrochlores, **Jasmeet Kaur Gill**, O.P. Pandey and K. Singh, FUCETECH 2011.