STUDY OF PHYSICAL STRUCTURAL AND THERMAL PROPERTIES OF CALCIUM BOROSILICATE GLASS SEALANTS

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Dedicated to my parents

CERTIFICATE

This is to certify that Ms. RUPALI GUPTA, Roll No. 30704016 *has worked on the thesis entitled "STUDY OF PHYSICAL STRUCTURAL AND THERMAL PROPERTIES OF CALCIUM BOROSILICATE GLASS SEALANTS" in the partial fulfillment for award of the degree of MASTERS OF SCIENCE in physics. I certify that the matter embodied in this report is of candidate's own record and not submitted to any other university in any part or full form for the award of such kind of a degree.*

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ABSTRACT

Planar design of Solid Oxide Fuel Cell (SOFC) is better than tubular design due to its higher current density and simple manufacturing. However, the planar design of SOFC requires sealants at the edges of the cells to prevent fuel leakage and air mixing at higher temperature. The glass and glass ceramics are most suitable and compatible with other components of SOFC at working temperature of SOFC (800-1000°C). In the present study a series of SiO_2-B_2O_3-CaO-A_2O_3 (A= La, Y) compositions have been synthesized by taking appropriate proportion (mol %) of each oxide constituents. Mixture of these components were heat treated for different time durations and then characterized by using various techniques viz X-Ray diffraction (XRD), Fourier Transform Infra Red spectroscopy (FTIR) and dilatometry to determine the possible reaction phases and prominent band formation. Amorphous nature of all the cast samples is confirmed by x-ray diffraction. During heat treatment main phase formed was La_2SiO_5. The FTIR spectra of all the samples exhibit three bands i.e, 400-600 cm^{-1} , 650-800 cm^{-1} and 800-1300 cm^{-1}. Transmission bands of all glass samples are composed of silicate and borate chains. The dilatomtery analysis were done to find the thermal expansion coefficient (TEC) and stability respectively. In order to understand the crystallization kinetics these samples were heat treated at 900°C for various heat treatment durations. A detailed structural, thermal and properties of calcium borosilicate glasses has been presented in this report.

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LIST OF ABBREVIATIONS

SOFC	Solid Oxide Fuel Cell
PAFC	Phosphoric Acid Fuel Cell
AFC	Alkaline Fuel Cell
PEMFC	Proton Exchange Membrane Fuel Cell
DMFC	Direct Methanol Fuel Cell
MCFC	Molten Carbonate Fuel Cell
XRD	X-Ray Diffraction
FTIR	Fourier Transform Infra Red
TEC	Thermal Expansion Coefficient
YSZ	Yttria Stabilized Zirconia

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CHAPTER – 1
INTRODUCTION

1.1 FUEL CELL

The modern scientific and technological approach, in the area of energy production is to develop inexpensive devices, which could satisfy the current device for cleaner and more efficiently distributed power, particularly in combination of heat and power systems. In this context, the recent flurry of activity by the scientific and engineering community has brought the fuel cell into the public eye. Fuel cells represent a promising and viable alternative for large scale generation of electricity, with minimal undesirable chemical, thermal and acoustic emissions. A fuel cell is a device that directly converts the chemical energy of reactants (a fuel such as hydrogen, natural gas, methane or methanol and oxygen) into electricity. It is an electrochemical device that contains two electrodes (an anode and cathode) and an electrolyte; it uses a chemical reactant to produce electricity much like battery. However, unlike a battery, a fuel cell never “goes dead” and never needs recharging. It will continue to produce power as long as it has a constant supply of fuel and oxygen. Fuel cells are currently attracting tremendous interest because of their huge potential for power generation in stationary, portable and transport applications and our increasing need for sustainable energy resources. The combination of the high efficiency with which chemical energy is converted directly into electrical energy, and the very much lower emissions of sulphur and nitrogen oxides and hydrocarbon pollutants, and significantly reduced CO_2 emissions, confers very significant environmental advantages on fuel cells over conventional power generation. However, significant advances in the development of both materials with improved properties and in manufacturing processes in the last two decades have made fuel cells a realistic proposition to compete on a commercial footing with conventional power generation.

The concept of the fuel cell was first demonstrated in 1839 by William Grove [1] and was known as the father of the fuel cell. While investigating the electrolysis of water, Grove observed that when the current was switched off, a small current flowed through the circuit in the opposite direction, as a result of a reaction between the electrolysis products, hydrogen and oxygen, catalyzed by the platinum electrodes. Ceramics fuel cells came into existence much later and began with Nernest’s discovery of solid-oxide electrolytes in 1899 and the operation of the first ceramic fuel cell at a temperature of 1000^0C was demonstrated by Baur and Pries in 1937. In their experiment they used zirconium, yttrium, cerium, lanthanum and tungsten as electrolytes, with little success [2]. Much of the research, however, was short-lived as melting, short circuiting, and high electrical resistance inside the cell materials created numerous technical hurdles. Their designs were not as good to provide electrical conductivity up to the mark as was expected due to unwanted chemical reactions between the electrolytes and various gases, including carbon monoxide. By the late 1950's, research into solid oxide technology began to accelerate because of advancement in ceramic processing [3].

1.2 TYPES OF FUEL CELLS

Fuel cells technologies can be classified in manyways, for example by temperature, fuel type [4] and charge carrier. However, the most common classification is according to the type of electrolyte used. This determines the kind of chemical reactions that take place in the cell, the kind of catalysts required, the temperature range in which the cell operates, the fuel required, and other factors. These characteristics, in turn, affect the applications for which these cells are most suitable. There are several types of fuel cells currently under development, each with its own advantages, limitations, and potential applications. The main focus of research on fuel cells is now to improve fuel cell behaviour with regard to:

- Operating temperatures
- Lifetime
- Catalytic or conductivity efficiencies
- Or simply manufacturing issues by using different materials in electrodes and electrolytes

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Based on the type of electrolyte used there are a number of different types of fuel cells, and each offers its own operating characteristics and application opportunities. Fuel cells can be categorized as:-

(1) Proton Exchange Membrane Fuel Cell (PEMFC)
(2) Alkaline Fuel Cell (AFC)
(3) Phosphoric Acid Fuel Cell (PAFC)
(4) Molten Carbonate Fuel Cell (MCFC)
(5) Direct Methanol Fuel Cell (DMFC)
(6) Solid Oxide Fuel Cell (SOFC)

The above are numerous types of fuel cells that have been made. The most common are shown below in table 1.1. Each type uses different materials and operates at different temperature [5].

Table 1.1: Technical details of various fuel cells.

Type	Abbreviation	Operating temp	Uses
Solid Oxide	SOFC	500-1000^{0}C	All sizes of CHP
Direct Alcohol	DAFC	50-100^{0}C	Buses, cars, appliances, small CHP
Polymer Electrolyte	PEFC	50-100^{0}C	Buses, cars
Phosphoric Acid	PAFC	200^{0}C	Medium CHP
Molten Carbonate	MCFC	600^{0}C	Large CHP
Alkaline	AFC	50-250^{0}C	Used in space vehicles

1.3 SOLID OXIDE FUEL CELL (SOFC)

Solid oxide fuel cells (SOFCs) use a hard, non-porous ceramic compound as the electrolyte. It is highly promising fuel cell; this type could be used in high power applications including industrial and large-scale central electricity generating stations. Some developers also see SOFC use in motor vehicles and are developing fuel cell auxiliary power units (APUs) with SOFCs [6, 7]. It is considered to be the most desirable fuel cell for generating electricity from hydrocarbon fuels due to tolerant to impurities, and can at least partially internally reform hydrocarbon fuels. Power generating efficiencies could reach 60% and 85% with cogeneration and cell output is upto 100 kW in this fuel cell. One type of SOFC uses an array of meter-long tubes (tubular design), and other variations include a compressed disc planar design [8]. Tubular SOFC designs are closer to commercialization and are being produced by several companies around the world such as Siemens Westinghouse Cooperation which operates at 1000^{0}C. These long tubes have high electrical resistance but are simple to seal. Many companies are now working on a planar SOFC composed of thin ceramic sheets which operate at 800℃ or even less. Thin sheets have low electrical resistance and possible high efficiencies. Cheaper materials can be used at these lower temperatures.

The main disadvantage of SOFCs is the high operating temperature which results in longer start up times and mechanical/chemical compatibility issues. It requires significant thermal shielding to retain heat and protect personnel, which may be acceptable for utility applications but not for transportation and small portable applications. The high operating temperatures also place stringent durability requirements on materials.

The development of low-cost materials with high durability at cell operating temperatures is the key technical challenge facing this technology.

1.3.1 ADVANTAGES OF SOLID OXIDE FUEL CELLS

Advantages of this class of fuel cells include high efficiencies, long term stability, fuel flexibility, low emissions, and cost. A big advantage of the SOFC is that both hydrogen and carbon monoxide are used in the cell [9]. The solid oxide fuel cell (SOFC) represents a solid-state; high-temperature (600-1000℃) system eliminates many of the technical challenges, although different limitations arise. In general, a SOFC system is well suited for applications where a high operating temperature and a longer start up transient are not a limitation, or high amounts of CO impurities are present. The main advantages of the SOFC system include:

1) Tolerance to CO, because it is oxidized as a fuel, eliminating one of the main drawbacks of the PEM fuel cell.
2) High operating temperature greatly reduces activation polarization and eliminates the need for expensive catalysts.
3) Potential for internal reformation of hydrocarbons.
4) Potential for high hybrid system efficiencies (~80%).
5) Tolerance to a variety of fuel stocks.
6) High-quality waste heat generated is ideal for a cogeneration system.

CHAPTER – 2
SOFC AND ITS COMPONENTS

A single unit of SOFC consist four layers stacked together is typically only a few millimeters thick. Hundreds of these cells are then connected in series to form what most people refer to as an “SOFC stack.” The ceramics used in SOFCs do not become electrically active until they reach very high temperature and as a consequence the stacks have to run at temperatures ranging from 600 to 1000℃. Reduction of oxygen into oxygen ions occurs at the cathode. These ions can then diffuse through the solid oxide electrolyte to the anode where they can electrochemically oxidize the fuel. In this reaction, a water by product is given off as well as two electrons. These electrons then flow through an external circuit. The cycle then repeats as those electrons enter the cathode material again.

2.1 SOFC DESIGN CONCEPTS

Two most important design configurations for SOFCs have emerged: a planar design and a tubular design. The two main types of designs are discussed below:

2.1.1 Planar design

In the planar design, the components are assembled in flat stacks, with air and fuel flowing through channels built into the cathode and anode. Compact stacks thus have minimal ohmic losses and a high power density as compared to other designs of SOFCs. The most straightforward type of design for a fuel cell is the planar design as shown in Figure 2.1.

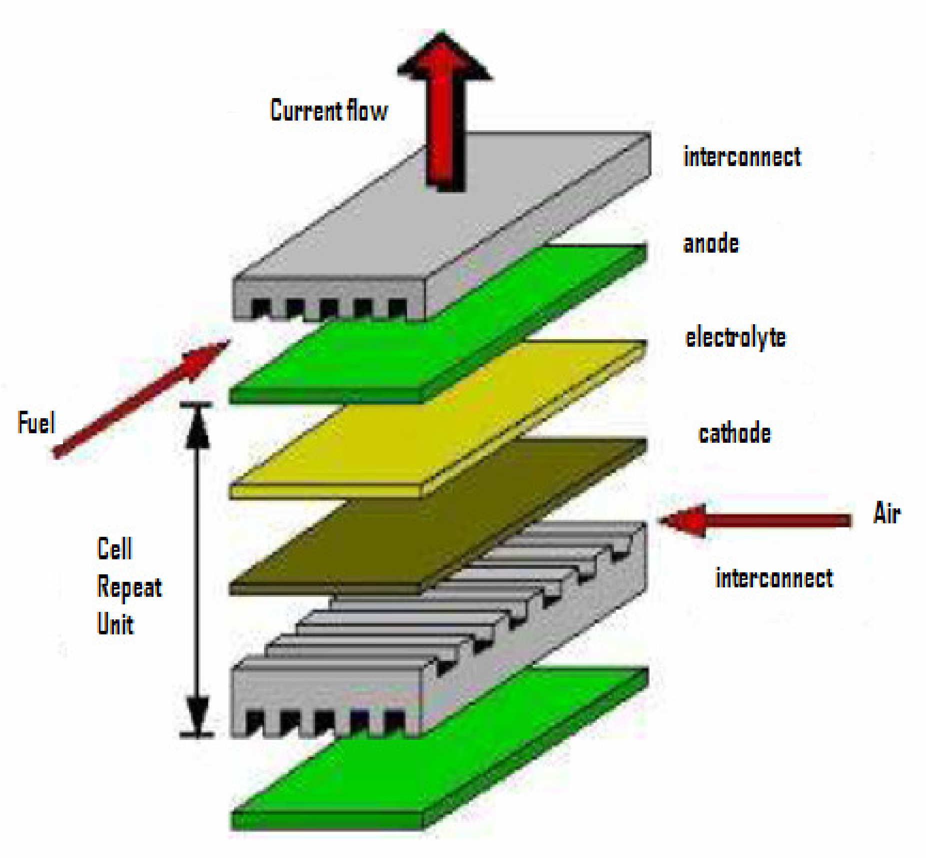

Fig 2.1: Configuration for a planar design SOFC.

However, the planar design has the major drawback of necessitating a sealing agent to prevent gases from leaking and let them properly flow in their respective channels [11]. Compressive, glass, cermets, and glass-ceramic seals have been used. Sealing is still a key issue in planar SOFC design, because it is difficult to maintain system integrity over the large thermal variation and reducing/oxidizing environment. Other disadvantages are the extreme brittleness in tension of the system, as the tensile strength of typical planar cells is 20% of their compressive strength, but also the possibility that the failure of one single cell may result in the failure of the whole stack. Thermal cycling and thermal stresses are also a major issue, due to the thinness of the materials used, which leads to research on temperature variations while the fuel cell is in operation. State of the art planar SOFCs use a thick anode as a support for a thin film electrolyte, which allows for a robust yet simple and compact design.

2.1.2 Tubular design

The design, and probably the most advanced, is the seal-less tubular concept pioneered by Westinghouse (now Siemens-Westinghouse) Company, USA. In the tubular design, components are assembled in the form of a hollow tube, with the cell constructed in layers around a tubular cathode; air flows through the inside of the tube and fuel flows around the exterior. The major advantage of this design is that the problematic high-temperature seals needed for other SOFC designs are eliminated. Tubular designs have been tested in 100 kW atmospheric pressure and 250 kW pressurized demonstration systems with little performance degradation with time. The tubular design of SOFC is shown in Figure 2.2.

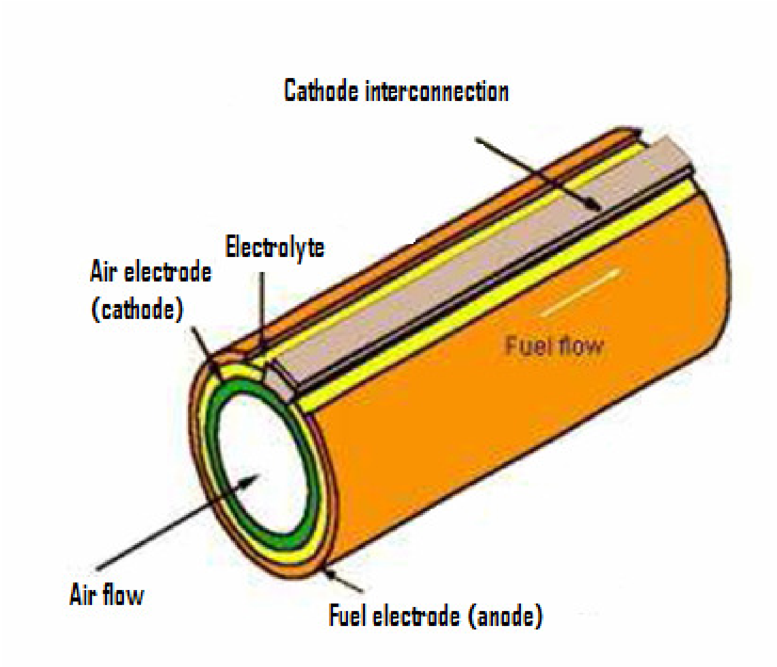

Fig 2.2: Configuration for a tubular design SOFC.

One drawback of this type of tubular design is the more complex and limited range of cell fabrication methods [10,11]. Another drawback is high internal ohmic losses relative to the planar design, due to the in-plane path that electrons must travel along the electrodes to and from the cell interconnect. This design can also experience significant losses due to limited oxygen transport through the porous (~35% porosity) structural support tube used to provide rigidity to the assembly. The most obvious one is the high production cost, as the process to fabricate a cylindrical tube of zirconia and to deposit metals on both sides, chemical vapour deposition (CVD) is carried out in a vacuum chamber.

The performance of the planar design is currently better than the performance of the tubular design because the planar design has a lower resistance comparatively. However, planar design must overcome an important challenge which does not apply to tubular system. In case of planar SOFC design, one of the most critical materials is the gas seal that must be applied along the edges of each cell and between the stack and gas manifolds. Glass and glass ceramics meet most of the requirements required for sealing at high temperature. Formation, properties and other details of glass and glass sealants, which are required for sealing in planar design of SOFC, will be presented in next chapters.

2.2 MATERIAL PROCESSING AND SELECTIONS

The materials for different cell components have been selected based on the following criteria [12]:

(a) Suitable electrical conducting properties required of different cell components to perform their intended cell functions.
(b) Adequate chemical and structural stability at high temperatures during cell operation as well as during cell fabrication.
(c) Minimal reactivity and inter diffusion among different cell components.
(d) Matching thermal expansion among different cell components.

2.2.1 Cathode (Air electrode)

The cathode, or air electrode, is a thin porous layer on the electrolyte where oxygen reduction takes place. The air electrode operates in an oxidizing environment of air or oxygen at 1000℃ and participates in the oxygen reduction reaction. The air electrode in solid oxide fuel cells has to meet the following requirements [12,13].

(a) High electronic conductivity.
(b) Chemical and dimensional stability in environments encountered during cell operation and during fabrication of interconnection, electrolyte and fuel electrode layers.

(c) Thermal expansion matches with other cell components

(d) Compatibility and minimum reactivity with the electrolyte and the interconnection with which air electrode comes into contact.

(e) Sufficient porosity to facilitate transport of molecular oxygen from the gas phase to the air electrode /electrolyte interface.

Cathodes are generally made of lanthanum compounds. $LaMnO_3$ is a p-doped perovskite structure which can undergo atomic distortion changing the shape of unit cells [14]. It can easily acquire excesses or deficiencies in either lanthanum or oxygen, making it easy to match the substrate crystalline structure. However particular attention must be given to temperature variations as they are a major factor in the appearance of those defects. $LaMnO_3$ has intrinsic cation vacancies resulting in its p- type nature. Its conductivity can be further enhanced by replacing some atoms with lower-valence cations such as strontium, barium, nickel, magnesium or calcium. Strontium has currently proved to be the best dopant under oxidizing conditions. The substitution of La^{3+} with Sr^{2+} allow for a higher concentration of Mn^{4+} ions favouring conductivity. Furthermore, the reactivity and inter diffusion studies between doped lanthanum manganite and yttria stabilized zirconia electrolyte have shown any interactions between these two materials at 1000℃ to be minimal. Other materials of the same class as $LaMnO_3$ are investigated, such as $LaCoO_3$, which has large oxygen deficiencies at high temperatures. This particular compound has a better conductivity under similar conditions, but is much less stable against reduction reactions. Tin-doped Indium Oxide has also been considered but was deemed too costly. For SOFC substantially operating at lower temperature, such as 600-800℃, alternative cathode material has been developed and optimized since $LaMnO_3$ does not appear to be a satisfactory choice at lower temperature, owing to its low ionic conductivity and slower oxygen transfer kinetics. For these cases other pervoskite structure materials such as containing Co, Fe or Ni has received greater attraction but there are certain limitations such as TEC mismatching of Co with electrolyte, and electrical conductivity of Fe is low but promising results has been obtained by using these materials.

2.2.2 Anode (Fuel electrode)

The ceramic (anode) layer must be very porous to allow the fuel to flow towards the electrolyte. Like the cathode, it must conduct electrons, with ionic conductivity a definite asset. The most common material used is a cermet made up of nickel mixed with the ceramic material that is used for the electrolyte in that particular cell, typically YSZ (yttria stabilized zirconia), where the excellent electrical conductivity of nickel is combined with a porous YSZ powder and sintered at 1400℃, resulting in a highly porous, conductive electrode with many three-phase contact points. There is a thermal expansion coefficient mismatch between nickel and YSZ causing cracks in either the electrode or the electrolyte material. Copper and cobalt are two other materials that are beginning to see a wider use in fuel cell anodes. Although copper, and cobalt even more so, are more expensive than nickel they still are a better candidates than platinum. These metals can also withstand the high temperatures of a SOFC without being oxidized. The anode is commonly the thickest and strongest layer in each individual cell, because it has the smallest polarization losses, and is often the layer that provides the mechanical support [11, 12].

The main function of the anode is to use the oxygen ions that diffuse through the electrolyte to oxidize the hydrogen fuel. The oxidation reaction between the oxygen ions and the hydrogen produces both water and electricity (release electrons to the external circuit). If the fuel is a hydrocarbon, for example methane, another function of the anode is to act as a catalyst for steam reforming the fuel into hydrogen [15]. This provides another operational benefit to the fuel cell stack because the reforming reaction is endothermic, which cools the stack internally.

2.2.3 Interconnector or separator

The interconnector can be either a metallic or ceramic layer that sandwitches between each individual cell. Its purpose is to connect each cell in series, so that the electricity each cell generates can be combined. Because the interconnector is exposed to both the oxidizing and reducing side of the cell at high temperatures, it must be extremely stable. For this reason, ceramics have been more successful in the long term than metals as interconnect materials. However, these ceramic interconnect materials are very expensive as compared to metals. Nickel- and steel-based alloys are becoming more promising interconnect materials as lower temperature (600-800℃). The most common intermetallic materials used today are doped lanthanum chromites. Ceramic-metal composites called 'cermet' are also under consideration, as they have demonstrated thermal stability at high temperatures and excellent electrical conductivity.

Interconnection serves as the electric contact to the air electrode and also protects the air electrode material from the reducing environment of the fuel on the fuel electrode side. The requirements of the interconnector are as follows: [12,13]

(a) Nearly 100% electronic conductivity.
(b) Stability in both oxidizing and reducing atmospheres at the cell operating temperature.
(c) Low permeability for oxygen and hydrogen to minimize direct combination of oxidant and fuel during cell operation.
(d) A thermal expansion close to that of the air electrode and the electrolyte.
(e) Non-reactivity with the electrodes, and easy to be fabricated.
(f) Low volatility and moderate cost.

As an alternative to ceramic interconnects, corrosion-tolerant conductive oxide scale forming commercial and experimental metallic alloys are also currently being investigated for use as current collectors in intermediate-temperature SOFCs. Metals and alloys offer the potential for lower cost, ease of fabrication and joining, excellent thermal conductivity, and commercial availability. Corrosion behaviors of Fe- and Ni-base alloys have been extensively studied under simulated fuel cell interconnect exposure conditions [16] and hence are less preferred.

2.2.4 Electrolyte

The electrolyte is a dense layer of oxygen ion conducting ceramic. Its electronic conductivity must be kept as low as possible to prevent losses from leakage currents. The high operating temperatures of SOFCs allow the kinetics of oxygen ion transport to be sufficient for good performance. However, as the operating temperature approaches the lower limit for SOFCs at around 600℃, the electrolyte begins to have large ionic transport resistances and affect the performance. Popular electrolyte materials include yttrium stabilized zirconia (YSZ) (often the 8% form 8YSZ), doped cerium oxide and doped bismuth oxide.

YSZ has emerged as the most suitable electrolyte material. Yttria serves the dual purpose of stabilizing zirconia into the cubic structure at high temperatures and also providing oxygen vacancies at the rate of one vacancy per mole of dopant. A typical dopant level is 10mol % yttria.

If the conductivity for oxygen ions in SOFC can remain high even at lower temperature (current target in research ~500˚C), material choice for SOFC will broaden and many existing problems can potentially be solved. The required properties for these materials, fixed by both electrochemical constraints and high operating temperature, are the following:

1. High ionic conductivity.
2. Phase stability from room temperature to 1000℃ approximately.
3. Thermal expansion coefficient compatible with other cell components.
4. Chemical compatibility with electrode and interconnection materials and with oxygen and fuel gas as well.
5. Moderate cost of materials and fabrication.

A thin, dense film of electrolyte (approximately 40 microns thick) needs to be applied to the cathode substrate. A reliable way to apply the electrolyte is known as electrochemical vapour deposition which offers high purity and a high level of process control. Electrochemical vapour deposition solves the problem of depositing a dense film onto a porous substrate by passing oxygen through the inside of the cathode tube while chlorides of zirconium and yttrium are passed along the outside. They react at the tube surface to form YSZ and, because the reaction comes to the surface from both sides, the porosity is closed off. Once the porosity is closed off, the electrolyte deposition continues, but now the oxygen diffuses through the growing YSZ layer to react with the chlorides, thereby ensuring a highly dense electrolyte layer [13, 14]. The process while effective is expensive and capital-intensive.

CHAPTER – 3

GLASS SEALANTS IN SOFC DESIGN

3.1 SEALANTS

One of the major challenges for implementation of solid oxide fuel cells (SOFCs) is the development of suitable sealant materials to separate the air and fuel. Several approaches have been used to achieve the necessary adherence, mechanical integrity and stability, including both rigid seals (no applied load during operation) and compressive seals (load applied to seal during operation). The most common approach is to use rigid glass or glass–ceramic seals, the properties of which can be tailored specifically for use in SOFCs through variation of the glass composition. However, these ceramic materials are inherently brittle, so metallic, metallic–ceramic and ceramic–ceramic composite seals, in both the rigid and compressive configurations, have been developed. The use of multiphase seals allows for improvement in factors, such as wettability, compliance at interfaces and strain relief, to improve the gas-tightness and stability of the seal. For SOFC applications, the functional requirements and materials selection parameters of the SOFC seal [18] are summarized in table 3.1:

Table 3.1: Required parameters of sealants for SOFC.

Mechanical	**Chemical**
• Hermetic/marginal leak rate • TEC matching • Acceptable bond strength or compressive loading requirement • Resistant to degradation due to thermal cycling/ thermal shock	• Long- term chemical stability under simultaneous oxidizing/ wet fuel environments • Long- term chemical compatibility with the adjacent sealing surfaces • Resistance to hydrogen embrittlement
Design/Fabrication	**Electrical**
• Low cost • Facile processing and high reliability with respect to forming a hermetic sealing • Design flexibility	• Non- conductive(non-shorting configuration)

3.1.1 Role of sealing material in SOFC

- To prevent mixing of fuel and oxidant within stack.
- To prevent leakage of fuel and oxidant outside the stack.
- Isolate electrically cells in stack.
- Provide mechanical bonding of the components.

3.1.2 Glass Sealants in SOFC Design

A family of sealant materials has been developed for use in the solid oxide fuel cell (SOFC) and in other applications in the temperature range of 800–1000℃. These materials are based on glasses and glass-ceramics in the SrO–La_2O_3–Al_2O_3–B_2O_3 –SiO_2 system. Various glass-ceramics were prepared based on the BaO–Al_2O_3–B_2O_3–SiO_2 system with the addition of La_2O_3, ZrO_2 or NiO in an attempt to develop a suitable sealant for planar solid-oxide fuel cells operating at 800℃. To estimate the applicability of these glasses as suitable sealants, their thermal and chemical stabilities as well as the crystallization behaviour and bonding characteristics of their parent glasses were investigated [19-22]. The thermal properties and crystallization behaviour of the parent glasses were dependent on the type of additive used, and the bonding characteristics were strongly influenced by the B_2O_3/SiO_2 value in the glass composition. The coefficients of thermal expansion (TEC) for these materials are in the range of 8–13 X 10^{-6}/℃, a good match with those of the SOFC components. These sealant materials bond well with the ceramics of the SOFC and more importantly, form bonds that can be thermally cycled [23] without failure. At the fuel cell operating temperature, the sealants have viscosities in the range of 10^4 –10^6 Pa-s, which allow them to tolerate a TEC mismatch of about 20% among the bonded substrates. The gas tightness of a sample seal was demonstrated in a simple zirconia-based oxygen concentration cell. Many glass seals are deigned to soften, and viscously flow above the SOFC operating temperature to provide hermetic seals by mechanical/chemical bonding. On cooling back down to operating temperature, the glass crystallizes to form a rigid, bonded seal [24, 25, 26].

Observation of micro structural change and chemical reaction at the glass-ceramic/electrolyte interface confirmed that the prepared glass-ceramics possessed long-term stability during heat treatment at the operation temperature for up to 1000 h.

Within the SOFC it is important that the fuel and air streams are kept separate and that a thermal balance should be maintained to ensure that the temperature of operation remains within an acceptable range. Several designs of SOFC have been developed to accommodate these requirements of glass sealants; one option is shown schematically in Figure 3.1 given below:

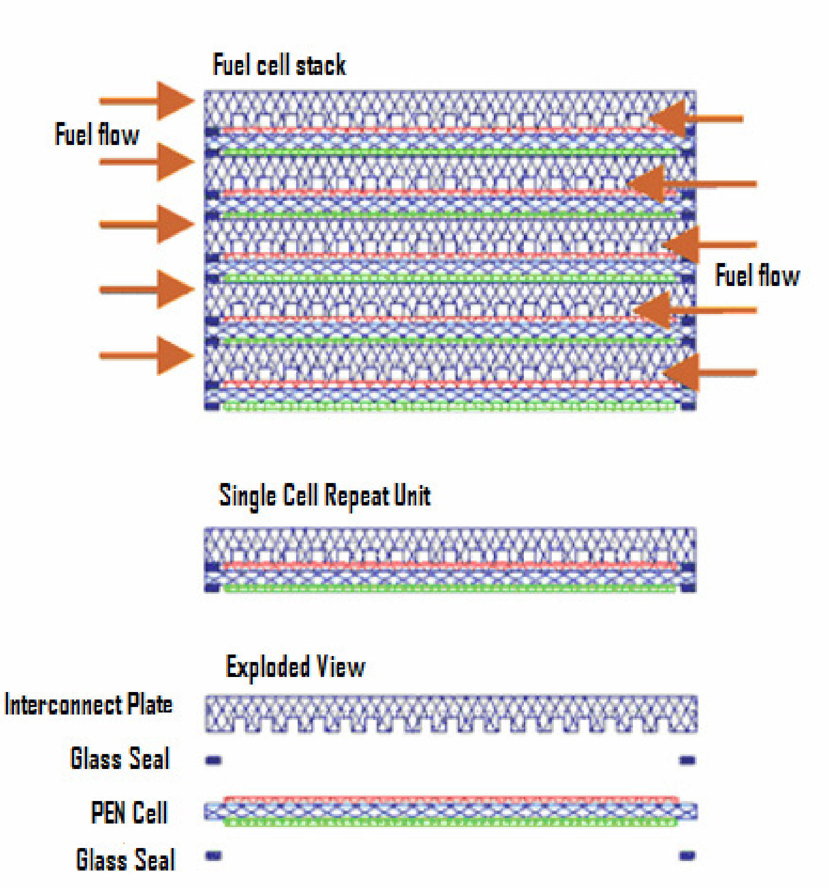

Fig 3.1: Glass sealants in planar design.

The requirement for effective, high temperature seals to prevent fuel leakage and air mixing at high temperature along with to seal the electrolyte against the metallic body of the device, in order to create a hermetic, rugged and stable stack is the urgent requirement of the planar design [Figure 2.1]. Any leakage of fuel into the air (or air into the fuel) will lead to direct combustion of fuel and may cause local overheating (hot spots) and sometimes may burst .It is necessary to seal the electrodes properly to prevent the fuel gas and air from mixing during the operation . The cathode is required to be sealed on the fuel inlet and outlet side while the anode is to be sealed on the air inlet and outlet side.

Typical conditions under which the SOFC is expected to operate and to which the seal will be exposed include [27]:

- An average operating temperature of 750°C.
- Continuous exposure to an oxidizing atmosphere on the cathode side and a wet reducing gas on the anode side.
- An average oxygen partial pressure in the range from 2×10^4 to 1×10^{-13} Pa.
- An anticipated device lifetime of more than 10,000 hours.

3.1.3 Current Status of Glass Sealant

A sealing material has to fulfil some critical requirements as described above, because the operation temperature of the SOFC is almost 850℃ and the operation period must be more than 5 years. Other major requirements are [28]:

- No chemical reaction with the joining components and solder stability in oxidizing and wet reducing atmospheres;
- Viscosity: 10^5 Pa-s at joining temperature (1000℃) and $>10^9$ Pa-s at operating temperature (850℃);
- Only a small thermal expansion mismatch with respect to SOFC components (TEC = $11 \mathrm{X} 10^{-6}$ K^{-1});
- Resistivity more than 2 k Ω cm^2;

However, several challenges remain with respect to the use of glass seals in SOFCs. The brittle nature of glasses below the glass transition temperature makes the seals vulnerable to crack formation, and glasses tend to react with other cell components, such as electrodes, at SOFC operating temperatures. Glass seals can affect electrode performance over a short range (via solid state diffusion or viscous flow) or over longer distances (via gaseous transport of glass constituents).Glass ceramics sealants are potential sealants because they can be tailored to optimize the physical properties and have greater resistance against corrosion as compared to other materials and are compatible with other components of SOFC.

3.1.4 Various glass- ceramics sealants systems

1. P_2O_5 Glasses - The main problem with these types of glasses is the volatization of the phosphate phase leading to surface nucleated crystallization. Meta or pyro-phosphate phases are formed which show poor stability at higher temperature in wet gas atmosphere. Thermal coefficient of expansion of phosphate does not match with YSZ.
2. B_2O_3 Glasses - These have low softening temperature and are volatile in nature. Alkali borosilicate is not suitable for large sealing area because of the thermal mismatching and also at higher temperature glass forming agent B_2O_3 is lost.
3. SiO_2 Glasses - These are the best available glass sealant. Alkali silicate glasses are not used because they interact with other components of fuel cell. Alkaline earth aluminosilicate glass sealants are generally used because of following properties:

- High resistivity
- High thermal expansion (matching TEC with other components)
- Glass ceramics

Table 3.2: Different glass sealing materials are summarized in tabular form as shown below.

Various glass systems	**Different features of glass systems**
P_2O_5 Glasses	Low TEC, low strength, reaction at anode, water soluble
B_2O_3 Glasses	Volatile, low softening temperature
SiO_2 Glasses	Best available glass sealants Alkaline earth aluminosilicate glass sealants

The most common sealants for SOFCs are glass or glass–ceramic materials, and have been shown to operate in fuel cells for more that 1000 h with no significant degradation. Many glasses and glass–ceramics generally used for sealants contain alkali metals. Although some alkali metal containing glasses have been used for sealants in SOFCs, they are generally avoided because they react with other fuel cell components and can enhance the volatility of chromium, which can lead to poisoning of the cathode. For SOFC applications, alkaline-earth-based glasses are more commonly used.

3.1.5 Problems with Glass Sealants

Potentially there are several ways in which a rigid glass seal can fail during operation, including the following:

- *Failure by fracture under pressure* - The glass seal can be viewed essentially as a multi component laminate composite composed of the electrolyte, the sealing glass and the oxide scale that naturally forms on the metal substrate during stack sealing and operation. Each of these layers is a brittle material and as such, each is susceptible to failure by brittle fracture. Thus, if a large enough flaw exists in any of the materials with in the seal or if the residual tensile stresses of a minimum critical value develop due to thermal expansion mismatch between components or warping due to non-uniform heating with in a given component, fracture can occur [29].

- *Failure during rapid thermal cycling* - Thermal gradients arising during rapid heating or cooling can generate out-of-plane bending stresses that may lead to failure in one of the brittle components in the ceramic-to-metal joint. In addition, thermal cycling may lead to fatigue problems in both the metals and ceramic components. Specifically in ceramic materials, this can occur due to a critical size under even small thermally generated stresses.

- *Failure upon thermal aging* - As the glass begins to crystallize, its carefully engineered thermal expansion properties will change and continue to evolve with time at operating temperature, which can ultimately limit the number of thermal cycles and the rate of cycling at which the joints are capable of surviving [30]. In addition, compositional and micro-structural changes induced by long term thermal diffusion are likely to take place at the seal/substrate interfaces, which may also lead to seal degradation and subsequent failure.

3.1.6 Criteria for selecting suitable Glass Sealant

Two important criteria for selection of a suitable glass sealant are the glass transition temperature (T_g) and the coefficient of thermal expansion (TEC). The glass transition temperature is important because the glass must flow sufficiently to provide an adequate seal, while maintaining sufficient rigidity for mechanical integrity. The coefficient of thermal expansion must match other cell components, such as the yttria-stabilized zirconia (YSZ) electrolyte and the interconnect material, to minimize thermal stresses. Most of the promising compositions are barium-containing glass–ceramics, which have relatively large coefficients of thermal expansion.

Different network formers, modifiers, intermediate and additives are used in it. The effect of all these variables on the properties of glasses has been considered as follows:

- **B_2O_3: SiO_2 ratio**

  B_2O_3/ SiO_2 ratio is a dominant factor in determining the glass transition temperature, T_g and the viscosity versus temperature behaviour of the glasses [31, 32, 33]. Glasses with high B_2O_3/ SiO_2 ratios have T_g at the lower end while those with low B_2O_3:SiO_2 ratios decrease glass transition temperature.
  Decrease in TEC of the glasses on increasing the SiO_2 content has also been reported by Lara et al.

- **Crystallization of glasses**

  The extent of crystallization is the major factor in the glass. Glass–Ceramics, which can be prepared by controlled crystallization of glass, possess superior mechanical properties and have very different thermal expansion coefficients (TEC), due to nucleation of different crystalline phases in different volume fraction. To develop a good sealant, it is therefore, necessary to understand the crystallization kinetics with other components of the cell [34]. In the case of calcium-containing glass ceramics for SOFCs, the crystallization increases thermal expansion. The crystallization in calcium glass ceramics for SOFC will increase the thermal expansion.

The crystallization of barium aluminosilicate glasses is faster than that of the corresponding calcium and magnesium aluminosilicate glasses. The lower activation energy for crystallization with barium as the network modifier has been attributed to the lower field strength of barium as compared to calcium and magnesium. Thus, barium aluminosilicate glasses crystallize more fully and at lower temperatures as compared to those based on other alkaline-earth cations. Conversely, insufficient crystallization may lead to inadequate mechanical properties.

- **Effect of additives**

  The properties of the sealants vary considerably by the use of several additives. The choice of additives is restrictive as they do not influence just one property of the sealant but they also have various side effects. Al_2O_3, for example, improves flux, thus making for better joining behaviour and too much Al_2O_3 decreases the thermal expansion, as it promotes the formation of a crystalline phase, which exhibit low thermal expansion coefficient. Similarly, Na_2O acts as the most effective flux, but it makes the glass soluble in water. Na_2O can be replaced by K_2O but the alkali cations react vigorously with the fuel cell components like cathode and form undesirable low TEC phases [32,33]. But on the other hand, addition of La_2O_3 and Y_2O_3 increases the thermal expansion coefficient and the transition temperature (T_g).

  Boron oxide is an important addition to silicate glasses. Boron oxide is most commonly added to decrease the viscosity of the glass, and has been shown to decrease the softening point and glass transition temperature of SOFC sealants. Boron oxide also increases the coefficient of thermal expansion, for compositions in which only the B_2O_3/SiO_2 ratio is changed. However, the effect of boron oxide on the coefficient of thermal expansion is overcome by other alloying additions for more complicated compositions. Boron oxide consistently leads to a decrease in the glass transition temperature.

CHAPTER – 4
EXPERIMENTAL TECHNIQUES

4.1 SAMPLE PREPARATION

Two glass compositions were prepared using melt quenching technique. The compositions of glasses are given in table 4.1. The powders of these glasses were placed in recrystallized alumina crucible for 1h, 10h heat treatment at 800° C to study the crystallization kinetics. The heat treated samples were taken out from the crucibles for various investigations such as X-ray diffraction (XRD) and Fourier Transform Infra-Red spectroscopy (FTIR).

Table 4.1: Glass compositions, sample name along with heat treatment duration.

Sample Name	Glasses	Heat treatment durations (h)
CaLa	CaO- SiO_2- B_2O_3- La_2O_3	1, 10
CaY	CaO- SiO_2- B_2O_3- Y_2O_3	1, 10

4.2 X-RAY DIFFRACTION TECHNIQUE (XRD)

X-ray diffraction analysis is the primary tool for investigating the structure of crystalline materials, their crystallite size and disordering. X-ray diffraction analysis (XRD) is a non-destructive, very versatile technique to determine the various crystallite phases, crystallographic structure and volume fractions of crystalline materials. The sample is irradiated with monochromatic X-ray and the reflected radiation is recorded by the counters. In this technique various forms of the samples could be used and very less amount is required for phase determination. The X-ray diffraction patterns were recorded using Rigaku model Geiger diffractogram with CuK_α radiation ($\lambda = 1.54$ Å) obtained from copper target using an in built Ni filter. The 2θ values for XRD patterns were generally taken in the range of 5 degree to 80 degree for most of the samples at a scan speed of 5 degree per minute Inter planar spacing (d) values of samples were calculated using the Bragg's law:

$$2d\sin\theta = n\lambda \qquad (1)$$

where λ is the wavelength of incident X-ray, d is the interplanar distance and θ is diffraction angle. The XRD patterns were identified using standard Powder Diffraction files (PDF).

4.3 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

Infrared (IR) spectroscopy is one of the most common spectroscopic techniques used to characterize organic and inorganic materials. Simply, it is the absorption measurement of different IR frequencies by a sample positioned in the path of an IR beam. The main goal of IR spectroscopic analysis is to determine the chemical functional groups in the sample. Using various sampling accessories, IR spectrometers can accept a wide range of sample types such as gases, liquids, and solids. Thus, IR spectroscopy is an important and popular tool for structural elucidation and compound identification. For most common materials, the spectrum of an unknown can be identified by comparison with known compounds. A simplified optical layout of a typical FTIR spectrometer is illustrated in Figure 4.1. IR absorption information is generally presented in the form of a spectrum with wavelength or wave number on the x-axis and absorption intensity or percent transmittance on the y-axis.

Fig 4.1: FTIR spectrometer.

4.4 DILATOMETRY

A dilatometer measures the expansion of a material when it is heated. A small material sample is placed into the instrument and then heated (or cooled) according to a schedule picked by the investigator.

4.4.1 Working Principle of dilatometry

In a dilatometer the dimensional change is measured by subjecting a sample to a change in temperature. In principle, one can devise a simple arrangement in which the movement is transmitted out of the controlled environments and into the ambient by holding the sample between two rods which extend outside of the heated region. The sample pushes the two rods (A and B) as it is being heated, hence the name "pushrod". By examining the experimental model, it becomes immediately clear that this configuration will not produce the desired ΔL_S. Since portions of both rods A and B are in the controlled environment, it is inevitable that they themselves will also expand (ΔL_A and ΔL_B respectively). Thus, the measured value of ($\Delta X_A+\Delta X_B$) will contain ($\Delta L_A+\Delta L_B$) in addition to ΔL_S. The sample's length change, ΔL_S, can therefore be written as:

$$\Delta L_S = (\Delta X_A - \Delta L_A) + (\Delta X_B - \Delta L_B) \ldots\ldots\ldots\ldots\ldots(2)$$

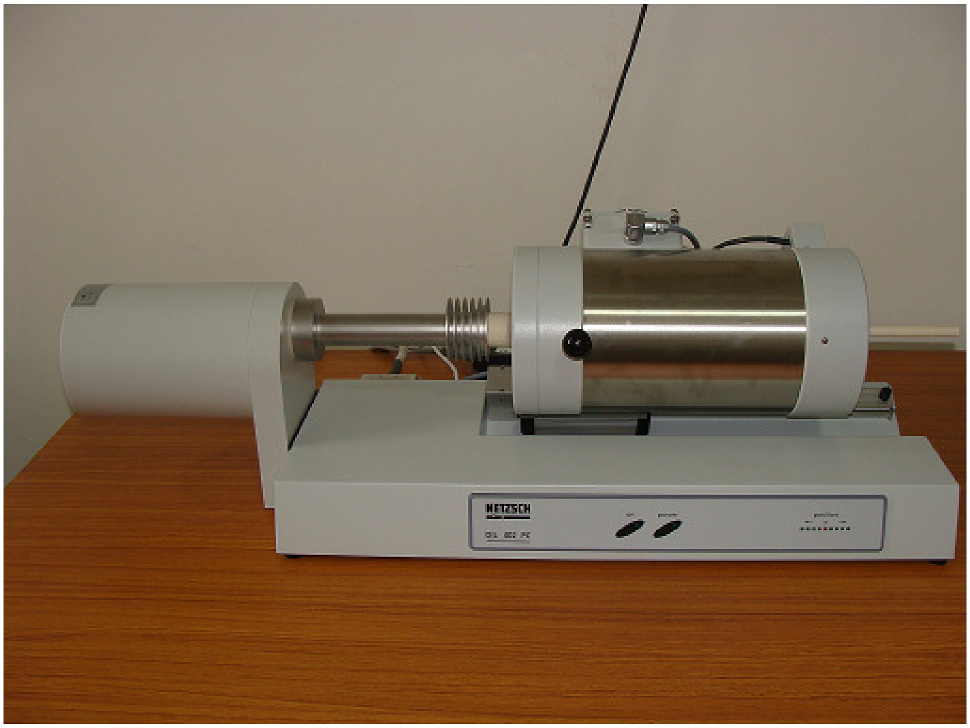

Fig 4.2: Dilatometer setup.

In general usage, however, one must determine the magnitude of ΔL_A and ΔL_B accurately. Most commonly, one tests a sample from a material already well-defined by some other absolute method (twin telescopes, interferometer, etc.), which then leaves only the combined values of ΔL_A and ΔL_B unknown. This process is known as "calibration" for the dilatometer; the welldefined material is referred to as a "standard" or "reference;" and the combined value of ΔL_A and ΔL_B and is known as "system correction."

A major drawback of this configuration is its susceptibility to errors due to transducer gain mis-adjustment or malfunctions. Additionally, the high magnification severely restricts the range of measurable displacement. For these reasons, the use of differential dilatometers should be limited to applications in which the advantages clearly outweigh these drawbacks.

If a temperature change from T_0 to T has caused this expansion in a sample of initial length L_0, the average coefficient of linear thermal expansion can be calculated as

$$a = (\Delta L_S / \Delta L_0) / (T - T_0) \ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

This coefficient, often referred to as TEC, is only true for the temperature range T_0 to T. (Note that the word "linear" should never precede the word "coefficient", as it always implies uni axial expansion rather than linearity of the coefficient.

CHAPTER – 5
RESULTS AND DISCUSSION

Glass–ceramics, as-prepared by controlled crystallization of glasses, exhibit superior mechanical properties than glasses and can have various TEC values depending on the type of precipitated crystalline phases and their volume fraction in the glass matrix. Glass–ceramics also show higher chemical stability than glasses, especially, under SOFC operating conditions. Therefore, in the present investigation, glasses were subjected to various heat - treatment, namely 1 and 10 h at 900^0C to study their crystallization behaviour and to examine any structural changes that may occur during prolonged thermal operation [35]. The formation of crystalline phases in glass matrix influence the long term behaviour of the sealant. For instance, the formation of cristobalite (SiO_2) and corderite phases are common in alumino silicate glasses. These phases are detrimental because they reduce the thermal expansion of the glasses which leads to the cracks in sealing materials.

5.1 THERMAL STABILITY

Thermo gravimetric analysis(TGA) provide fair idea about the thermal stability and phase transition of the subjected samples. The stability of the present glasses were measured using Diamond TG/ DTA (Perkin Elemer). The measurement was performed in the temperature range of 200 - 900°C in N_2 atmosphere. CaY glass sample exhibit higher weight loss than CaL glass samples as summarized in table 5.1. It may be attributed that glass matrix of CaL glass is more tightly bonded than CaY glasses. Our recent study on the similar glass shows higher fragility index of CaL glass as compared to the CaY glass [36].

5.2 X- RAY ANALYSIS

The heat treated samples are investigated using x-ray diffraction studies. XRD pattern of CaL and CaY samples are given in figures 5.1 and 5.2

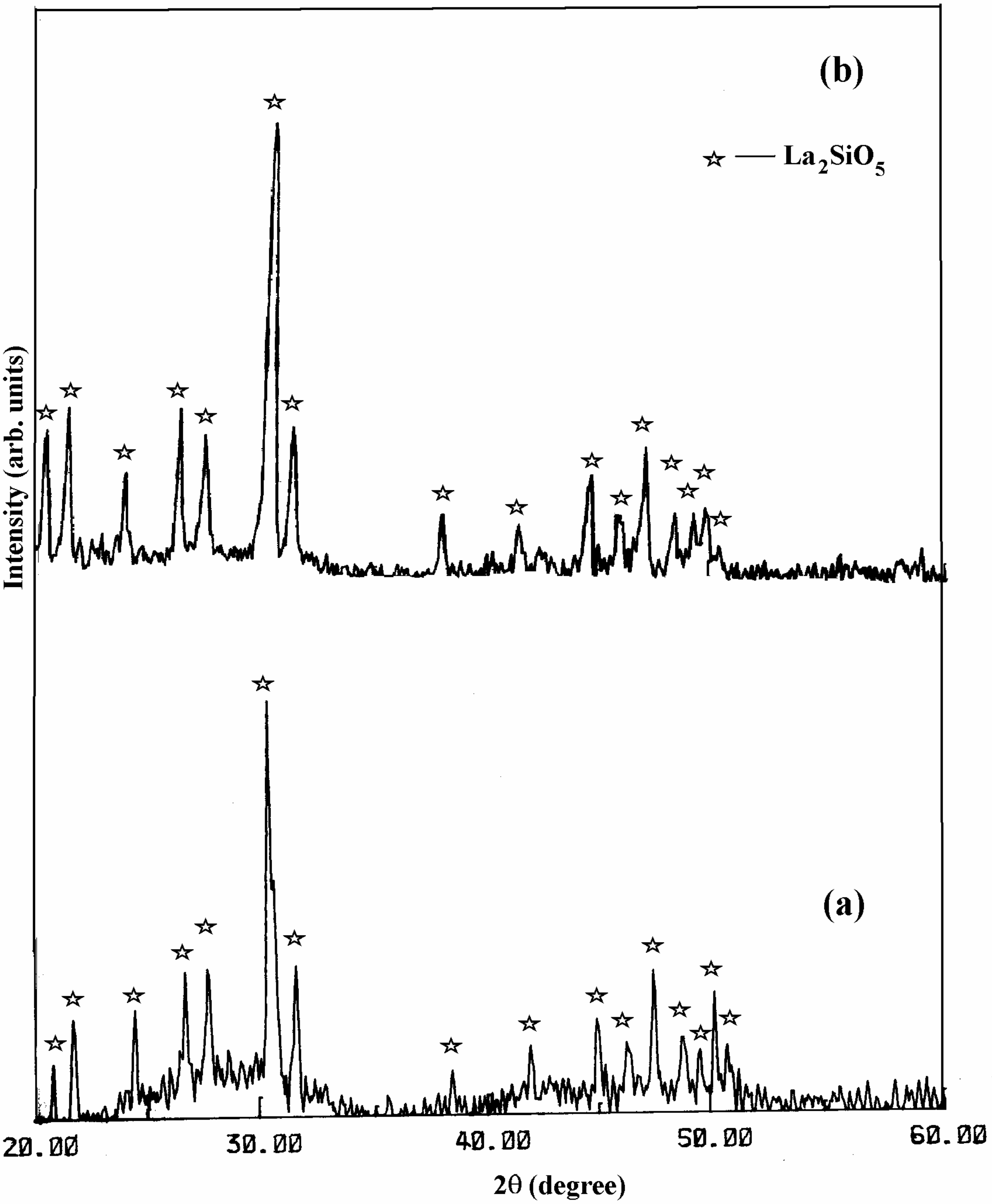

Fig 5.1: XRD pattern for sample CaL heat treated at (a) 1 h and (b) 10 h.

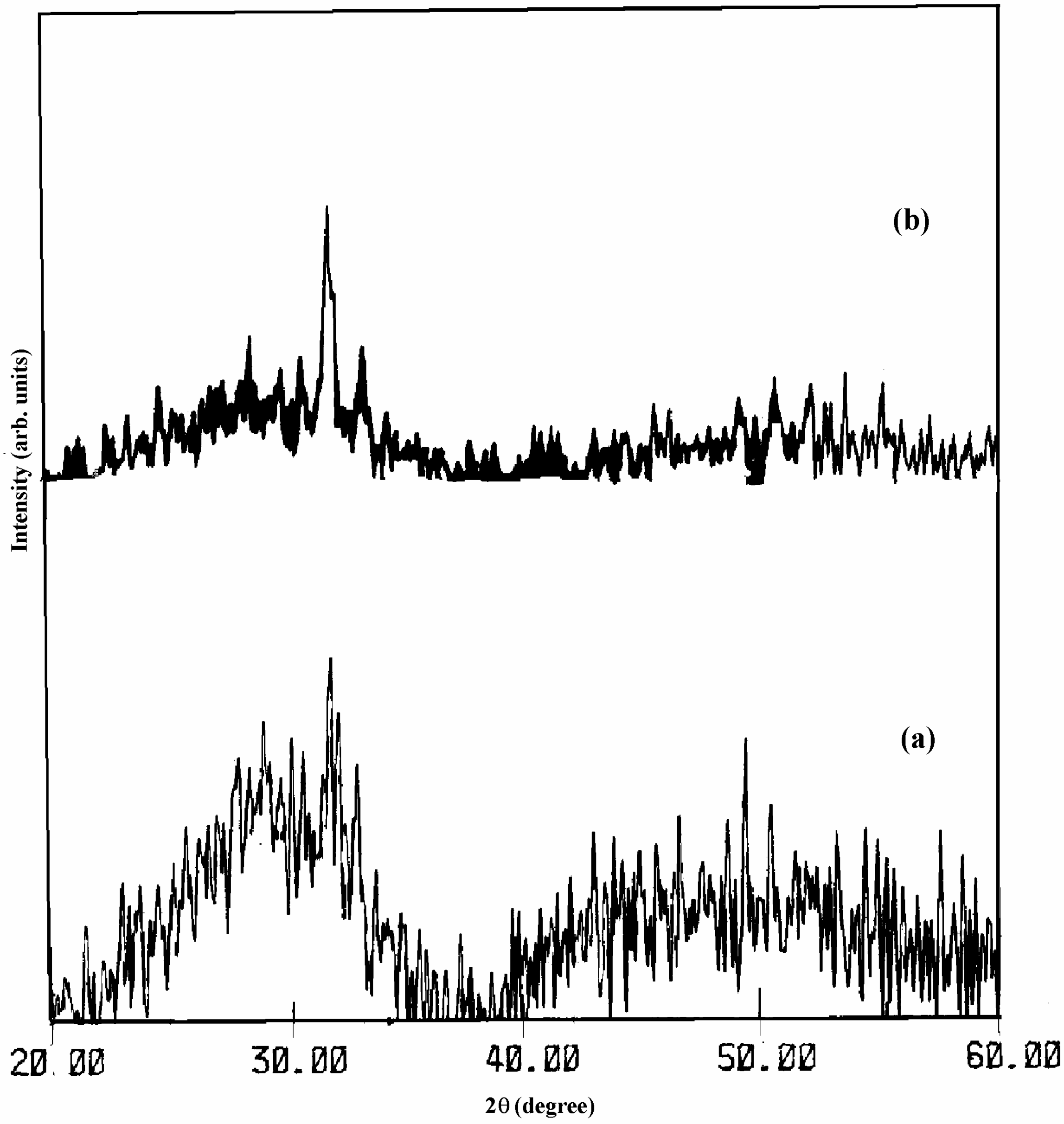

Fig 5.2: XRD pattern for sample CaY heat treated at (a) 1 h and (b) 10 h.

TABLE 5.1: Sample name, heat treatment duration along with crystallite size and full width of half maxima (FWHM)

Sample name	Heat treatment durations	Crystallite size (nm)	FWHM	Weight loss (%)
CaLa	1 h	22	0.33	0.2
CaLa	10 h	34	0.69	
CaY	1 h	NIL	NIL	2.7
CaY	10 h	NIL	NIL	

In the case of sample CaY, after 1 h heat treatment, the sample could not show the crystallization. As the heat treatment duration increases upto 10 h, very small change in XRD pattern is observed (Figure 5.2(b)). It means crystallization might be started in this sample. However, the crystalline phases could not fully grow. It might be possible that long duration of heat treatment leads to some crystalline phase formation in this particular sample. The CaY glass, has the highest glass transition temperature because of higher cross link density [37]. Due to this crystalline phase(s) did not form even after 10 h heat treatment as shown in Figure 5.2. It is possible that Y_2O_3 is associated with B_2O_3 instead of SiO_2 network former which may prevent formation of boron and yttria rich crystalline phases in this glass. Our earlier reports [37,38] also indicated that the addition of Y_2O_3 in any glass composition increase the glass transition temperature and prevent glass crystallization.

On the other hand, the CaL sample exhibit crystalline phase. The volume fraction of crystalline phase (La_2SiO_5) increases with increasing heat treatment duration from 1h to 10h. Interestingly, the XRD peaks become broader with progressive heat treatment. It might be attributed that La_2SiO_5 phase is nucleating during early stage of heat treatment in glass matrix. In later stage of heat treatment some other cations as Ca^{2+} could occupy some sites in La_2SiO_5 phase [39].The crystallite size for CaL glass composition were calculated using Schrerrer equation [40] as shown in table 5.1. The crystallite size increase from 22 nm to 34 nm as heat treatment duration increased.

5.3 FTIR ANALYSIS

Infrared spectra photometry was carried out on all samples to identify the functional groups present in these samples. In the spectra as shown in Figures 5.3 and 5.4 some of the peaks in the higher wave number region are due to the acetone group and others due to water molecules which is used during sample preparation. The major bands are assigned to silicate and borate groups which are present in higher mol% in the sample.

Generally, alkaline earth oxides (MgO, BaO, CaO, SrO) will not show any band in the IR spectra of silicate-borate glasses. However, their presence in sample shift the bands (especially, in the region 800-1300 cm^{-1}) towards higher or lower wave numbers. The shifting of bands towards lower or higher wave numbers depicts the connectivity in the glass structure (number of bridging oxygen, Q1, Q2...etc) [41]. All the FTIR spectra exhibit three broad transmittance bands i.e. 300-600 cm^{-1}, 600-800 cm^{-1} and 1300-1500 cm^{-1}.

These diffused bands indicate the general disorder in the silicate network mainly due to a wide distribution of Qn units (polymerization in the glass structure, where n denotes the number of bridging oxygen) occurring in these glasses. This change in bands might be associated with definite crystalline phases [42].

The bands in the 300–600 cm^{-1} region are due to bending vibrations of Si–O–Si linkages. The transmittance band in the 650–800 cm^{-1} region in the glasses is attributed to the bending vibrations of bridging oxygen between trigonal boron atoms and it is also related to the stretching vibrations of the A–O bonds with A^{3+} ions in four-fold coordination (A=Y, La). The band in the region 1350–1500 cm^{-1} corresponds to B–O vibrations in BO_3 triangle. Borate glasses show two characteristic bands derived from the B–O bonds in the BO_3 triangles about 1300–1500 cm^{-1} and the BO_4 tetrahedron about 1000 cm^{-1} [43]. These bands get shifted under the influence of surrounding cations, the extent and the direction of this shift depends on the type of cation. FTIR spectra of the glasses under investigation show that in these glasses boron primarily occurs in the form of BO_3 triangles (1396 cm^{-1}). However, the presence of BO_4 tetrahedron in the glass structure cannot be neglected. Since the IR band for BO_4 tetrahedron about 1000 cm^{-1} overlaps with that of stretching vibrations of SiO_4, therefore, it could not be observed [44].

The broad band in the 800–1300 cm^{-1} is assigned to the stretching vibrations of the SiO_4 tetrahedron with different number of bridging oxygen atoms [45, 46]. For heat treated glasses these bands shifts towards lower wave numbers implying towards the decrease in the connectivity of the silicate glass network.

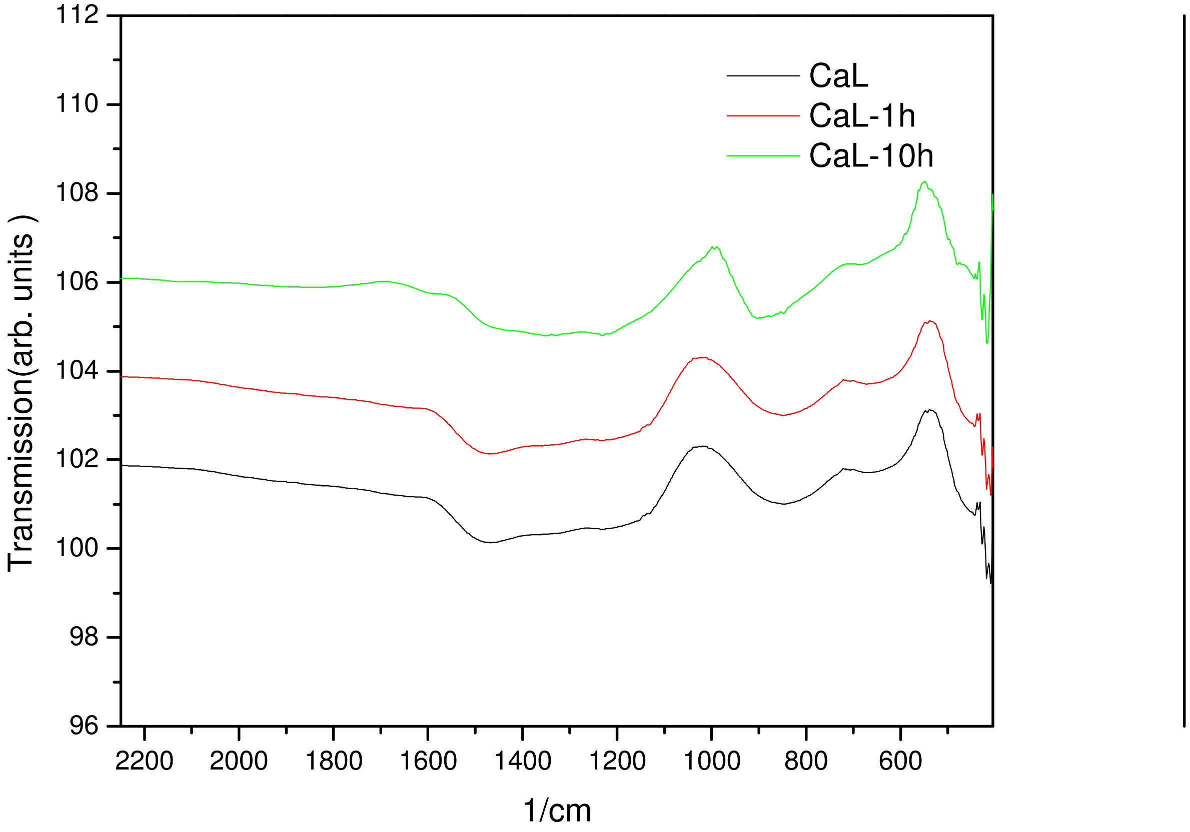

Fig 5.3: FTIR transmission spectra of CaL glass and glass ceramics.

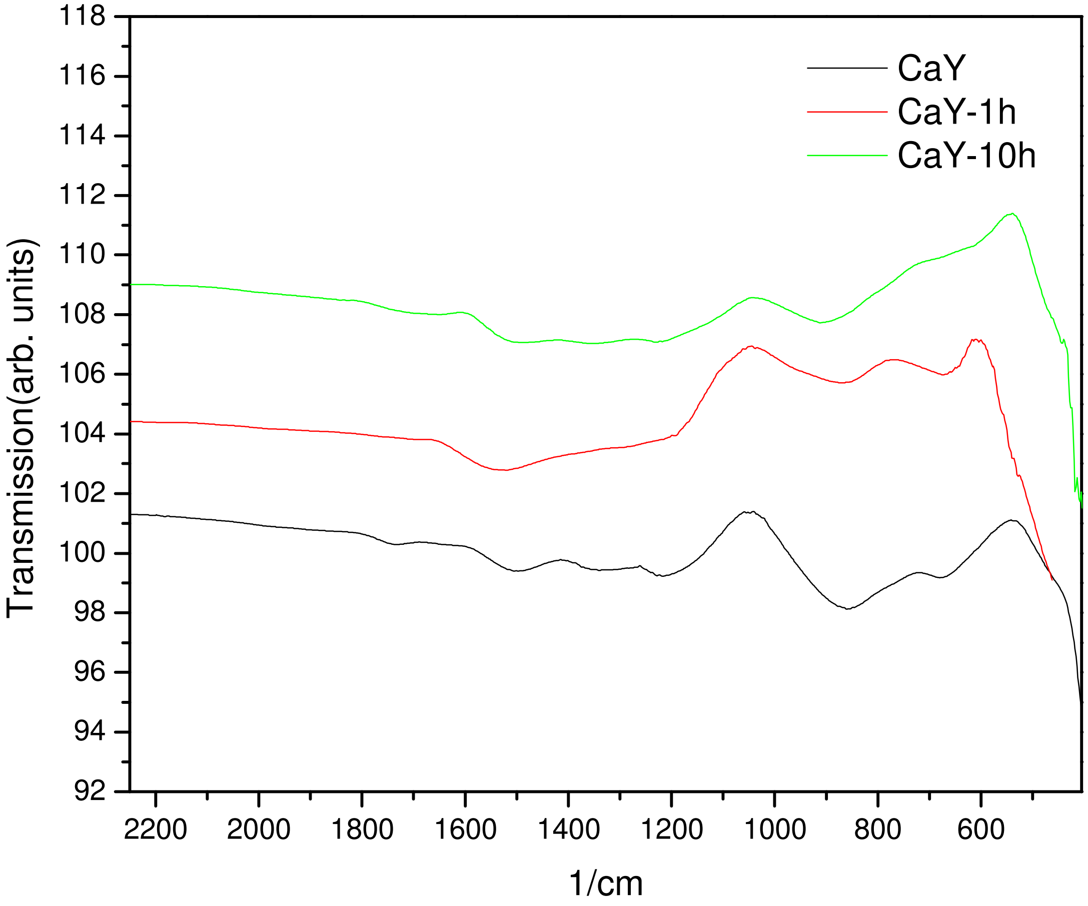

Fig 5.4: FTIR transmission spectra of CaY glass and glass ceramics.

The FTIR spectra of the CaL as shown in Figure 5.3, exhibit a transmission band in 460-650 cm^{-1} region which is attributed due to bending vibrations of the Si-O-Si and O-Si-O bending. The presence of a band in 750-820 cm^{-1} is due to the formation of Si-O-Si symmetric stretching of bridging oxygen. Apart from these bands the spectra of CaL band also show an 1120-1320 cm^{-1} which is due to boroxol rings and borate stretching. This band could be attributed to BO_4 stretching which shifts to lower wave number with increased heat treatment time duration. Another band is observed at 1328 cm^{-1} which is also due to boroxol rings and borate stretching. The 1450-1500 cm^{-1} transmission band corresponds to B-O vibrations of various borate groups and intensity of this band decreases as the time duration of heat treatment increases. The heat treatment duration could not show any appreciable change in spectra as shown in Figure 5.3. However, after 10h heat treatment the transmission peaks shift towards lower wave-number.

The transmission spectra of CaY glass shows band at 638-726 cm^{-1} due to the vibrations of oxygen between trigonal boron atoms. The next transmission band within the frequency range 814-982 cm^{-1} is due to Si-O^{-} stretching with two non- bridging oxygens. The transmission band in 1150-1240 cm^{-1} range and band at 1328 cm^{-1} is due to the presence of borate groups (tri-, tetra-, pentaborate groups). A transmission band is also present in 1450-1500 cm^{-1} frequency is due to the presence of B-O vibrations of various borate groups. A band at 1640 cm^{-1} is due to the presence of molecular water. The CaY sample could not show any change in various heat treated sample. So, no additional transmission band or peak is formed. However, the intensity of bands deceases in heat treated samples that was the only change in spectra. Additionally, after 10h heat treatment the transmittance peaks shift towards higher wave number.

As shown in Figure 5.4, the spectra of CaY glass and heat treated CaY sample shows continuous decrease in the intensity of the peaks as the time duration of heat treatment increases from 1 hr to 10 hrs is due to the bending vibrations of the Si-O-Si and Si-O-Y centred around 670.70 cm^{-1}. The peaks at 863.61cm^{-1} and 1215.45cm^{-1} is due to the Boroxol rings, tri-, tetra- and pentaborate groups pyro- and other borates (BO_3 stretching). There is a broad peak at 1499.33 cm^{-1} after 1 h heat treatment which might correspond to B-O vibrations of various borate groups (BO_3 stretching) and is clear from the spectra that this peak almost flattens as the time duration of heat treatment increase. The region 650- 800 cm^{-1} is the weak intensity region is having bending vibrations of Y-O bond almost centered around 723 cm^{-1} whose peak intensity increases with time.

In the calcium series of two glass samples, the CaY could not show any appreciable change in the FTIR spectra of glass (amorphous) and glass ceramics (1h & 10 h). Obviously, there is not too much change in the basic units. On the other hand CaLa sample show remarkable differences in glass and glass ceramic due to regrouping in Si-O-Si and BO_4 structure. Additionally, the shift of the bands at lower wave number in glass ceramic also indicates that these systems have more stability than their glass counterpart.

5.4 DILATOMETRY STUDY

Dilatometer measurements were carried out on glasses and glass ceramics in order to determine the thermal expansion coefficient (TEC) of the glasses. The TEC curve is shown in Figures 5.5 and 5.6. The purpose of this study was to know the effect of crystalline phases on the thermal expansion and comparison between TEC value of glass and glass ceramics. The results are summarized in table 5.2.

Table 5.2: TEC value of glass samples

Sample Name	**Glass TEC (X 10^{-6})**	**TEC Glass ceramic heated at 900^0C**	
		1 h	**10 h**
(CaL)	7.43	7.89	8
(CaY)	7.4	7.58	7.65

The CaL glass has higher TEC value among all the samples. The higher TEC in this glass as compared to CaY glass can be associated with the higher ionic radii of La^{3+} cations than Y^{3+}. Glass ceramics exhibit higher TEC than glasses which is due to the formation of crystalline phase which improve the TEC of this glass. CaY glass does not show much variation in TEC with heat treatment as very limited amount of crystallization has taken place in this glass. It indicates that this glass matrix could not change with heat treatment. The XRD results also support the TEC result of CaY sample.

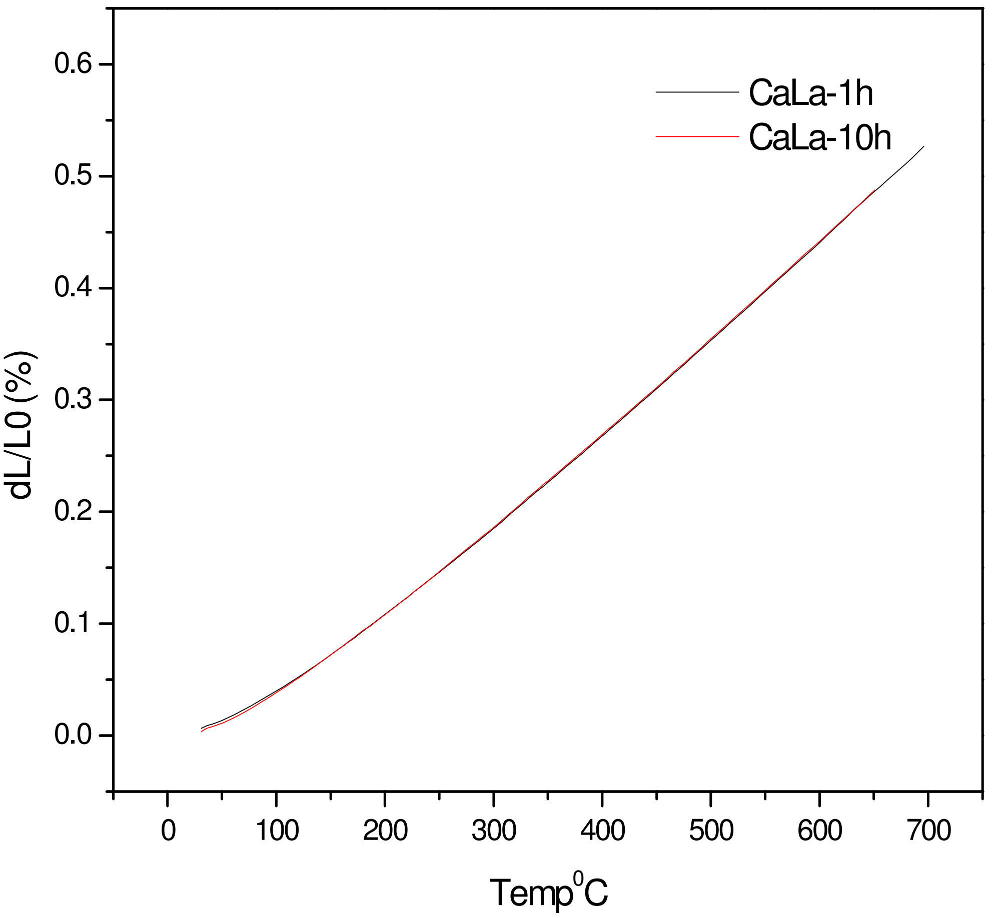

Fig 5.5: Dilatometry plot for CaL sample.

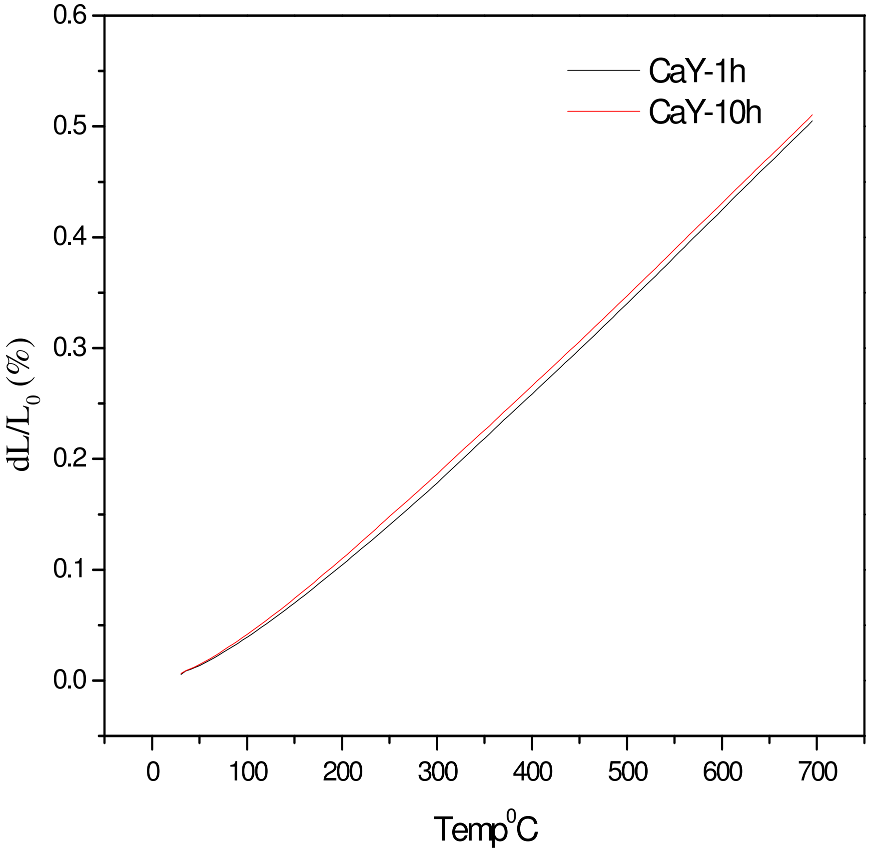

Fig 5.6: Dilatometry plot for CaY sample.

CHAPTER – 6

CONCLUSIONS AND FUTURE SCOPE

CONCLUSIONS

The main conclusions drawn from the present study are as follows:

- CaL glass is thermally more stable than CaY sample.
- In XRD study, La_2SiO_5 (monoclinic) phase is formed which is not detrimental for SOFC applications.
- The FTIR spectra of all the samples exhibit three bands i.e 550-630 cm^{-1}, 650-800 cm^{-1} and 800-1300 cm^{-1} which confirm the presence of silicate and borate network in the glass matrix.
- The thermal expansion coefficient of glass ceramics is higher as compared to parent glass. Hence, glass ceramics are better sealants. The TEC values of CaL sample is within limit which is required as a sealant (8-13 X 10^{-6}/ K).

FUTURE SCOPE

In order to study the long term behaviour of glass samples, it is essential to understand their crystallization kinetics at 850°, 900° and 950°C for longer duration (100 h). Furthermore, the reactivity of glasses with other components of SOFC should be studied for prolonged time durations so that their suitability can be checked as a sealing material. SEM can be carried out to study the morphological characters of the favourable as well detrimental phases. The SEM results can be correlated with other results.

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