

**Investigations on interfacial interaction of glass sealants
with electrolytes and interconnect for solid oxide fuel
cells**

A

Thesis

Submitted for the award of degree of

DOCTOR OF PHILOSOPHY

By

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Under the Guidance of

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(August-2012)**

*Dedicated
To My
Loving Sister*

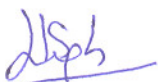
Declaration

I hereby certify that the work which is presented in thesis entitled “**Investigations on interfacial interaction of glass sealants with electrolytes and interconnect for solid oxide fuel cells**” in the partial fulfillment of the requirement for award of the degree of DOCTOR OF PHILOSOPHY in the School of Physics and Materials Science, Thapar University, Patiala, is an authentic record of my own work carried out under the supervision of Dr. Kulvir Singh and Dr. O. P. Pandey. The matter embodied in this report has not been submitted in part or full to any other university or institute for the award of any degree.


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This is to certify that the above statement made by the candidate is correct and true to the best of my knowledge.

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List of Publications

1. Influence of Y_2O_3 on structural and optical properties of $SiO_2-BaO-ZnO-xB_2O_3-(10-x)Y_2O_3$ glasses and glass ceramics, G. Kaur, M. Kumar, A. Arora, O.P. Pandey, K. Singh, **Journal of Non-Crystalline solids**, **357** (2011), 858-863.
2. Chemical interaction study between lanthanum based alkaline earth glass sealants with Crofer 22 APU for solid oxide fuel cell applications, G.Kaur, O.P. Pandey and K. Singh, **International journal of Hydrogen Energy**, **37** (2012), 3883- 3889.
3. Crystallization kinetics and thermal studies of calcium borosilicate glass sealants, V. Kumar, G. Kaur, O.P. Pandey, K. Singh, **Physics & Chemistry of Glasses**, **52** (2011), 212-220.
4. Thermodynamic stability of yttrium alkaline earth borosilicate glasses and their compatibility with Crofer for SOFC, G. Kaur, V. Kumar, O.P. Pandey, K. Singh, **Journal of Electrochemical Society**, **159** (2012), B277-B284.
5. Interfacial study between high temperature $SiO_2-B_2O_3-AO-La_2O_3$ (A= Sr, Ba) glass seals and Crofer 22 APU for solid oxide fuel cell applications, G. Kaur, O.P. Pandey, K. Singh, **International Journal of Hydrogen Energy**, **37** (2012), 6862-6874.
6. Assesment of *in-vitro* bioactivity of $SiO_2-BaO-ZnO-B_2O_3-Al_2O_3$ glasses: An optico-analytical approach, G. Kaur, P. Sharma, V. Kumar, K. Singh, **Materials Science & Engg. C** **32**(7), 1941-1947 (2012).
7. Optical, structural and mechanical properties of different valence cations doped bismuth vanadate oxides, G. Kaur, O.P. Pandey, K. Singh, **Physica status solidi-A**, **209** (7), 1231–1238 (2012).
8. Effect of modifier field strength on optical, structural and mechanical properties of lanthanum borosilicate glasses, G. Kaur, O.P. Pandey, K. Singh, **Journal of Non-Crystalline Solids** (DOI: 10.1016/j.jnoncrysol.2012.06.006).
9. Thermal, electrical and structural properties of $Bi_2V_{1-x}Ti_xO_{5.5-\delta}$ ($0.05 \leq x \leq 0.20$) oxide ion conductors, G. Kaur, O.P. Pandey, K. Singh, **Physica status solidi-A** (Minor revision).
10. Interaction of $MgO-SiO_2-B_2O_3-La_2O_3$ glass sealant with low temperature and high temperature electrolytes for SOFC applications, G. Kaur, O.P. Pandey, K. Singh, **International Journal of Hydrogen energy** (In press).
11. Glass stability and effect of heat-treatment duration on chemical interaction between calcium lanthanum borosilicate glass sealant and electrolytes, G. Kaur, O.P. Pandey, K. Singh, **Journal of Electrochemical Society** (DOI: 10.1149/2.043211jes).

12. Microstructural analysis of interfaces between lanthanum contained glass and two different electrolytes for SOFC applications, G. Kaur, O.P. Pandey, K. Singh, **Fuel Cells (In press)**.
13. Self-healing behavior of barium lanthanum borosilicate glass and its compatibility with high/low temperature electrolytes for SOFC applications, G. Kaur, O.P. Pandey, K. Singh, **International Journal of Applied Ceramic Technology (submitted after revision)**.
14. Non-equilibrium effects for RO-SiO₂ glass system using Jackson-Hunt and TMK model, G. Kaur, O.P. Pandey, K. Singh, (IN PIPELINE).
15. Macroscopic examination of meyer thermodynamic compensation rule for silica glasses (IN PIPELINE).

Conferences attended

1. Attended Conference on International Symposium on Fuel Cells, Fucetech 09, held from 7-9 nov. 2010, Mumbai.
2. Poster presentation on “Chemical interaction study between lanthanum based different alkaline earth glass sealants with Crofer 22 APU for solid oxide fuel cell applications”, (G. Kaur, O.P. Pandey, K. Singh), International Conference on Renewable energy, ICRE 2011, held from 17-21 January 2010, Jaipur.
3. Poster presentation on “Chemical compatibility of borosilicate glasses with Crofer 22 APU for SOFC applications”, (G. Kaur, O.P. Pandey, K. Singh) at IC2E4MCI-11 held from 19-12-2011 to 22-12-2011 in Agra (**won best poster award**).
4. Poster presentation on “Chemical compatibility of borosilicate glasses with yttria stabilized zirconia (YSZ) for SOFC applications”, (G. Kaur, O.P. Pandey, K. Singh) at 23rd AGM-MRSI held from 13-02-2012 to 15-02-2012 in Thapar University, Patiala (**won best poster award**).

Preface

Lots of research has been carried out to develop proper sealing materials for planar design of solid oxide fuel cell (SOFC). Rigid seals like glass and glass ceramics particularly alkaline earth containing are the most preferred sealant materials as they can sustain in stringent operating conditions of SOFCs. In addition to this, the properties of glasses can be tailored by selecting proper initial constituents and processing conditions. During SOFC operation, glass gets converted into glass ceramics due to formation of crystalline phases. Moreover, the interaction of glass sealants with different components of SOFC can also form different crystalline phases due to interdiffusion of anions and cations. Sometimes, these formed phases are very detrimental and cause deterioration of SOFC stack. Therefore, it is very important and essential to understand the crystallization kinetics of glass seals during interaction with other components of SOFC.

Based on literature survey, a series of glass composition was selected and synthesized and studied. The present work deals with the synthesis, characterization and compatibility of $\text{AO-SiO}_2\text{-B}_2\text{O}_3\text{-La}_2\text{O}_3$ (A= Mg, Ca, Sr, Ba) glasses with Crofer 22APU, TBV and YSZ. The entire work in this thesis is presented in **six chapters**.

Chapter 1 gives the description and background of fuel cells along with their comparative study. In addition to this, the role of sealants for planar SOFC stacks has been discussed. The importance of glass sealants, their processing conditions and effect of its constituents on various properties has been discussed. The present section also summarizes the interfacial interaction among glass seals and various components of SOFC.

Chapter 2 summarizes the current research in the area of interaction study among the sealants and various components of SOFC like electrolyte and interconnects. Bismuth vanadates being one of the promising low to intermediate temperature range electrolyte, have also been studied to elucidate the most promising electrolyte system for interaction with glasses. The last section of this chapter presents the gaps in the study so far with aims and objectives of the work of the thesis.

Chapter 3 gives the details of the experimental route followed for materials processing and characterization followed during the course of the present investigation. Glasses and electrolytes were prepared using conventional melt-quenching techniques and solid-state reactions respectively. Differential thermal analysis (DTA) and dilatometry were used for the measurement of thermal properties and characteristic parameters of glass sealants as well

as the synthesized low temperature electrolytes. X-ray diffraction (XRD) was used to confirm the amorphous nature of glass and to get information about the various phases formed during different heat-treatments. Scanning electron microscopy (SEM) was used for the microstructural analysis. In addition to this, electron probe microanalysis (EPMA) and X-ray dot mapping techniques were also used to know the concentration as well as segregation of elements. Two-probe method was used to measure the conductivity of samples. Many optical techniques like Fourier transform infra-red (FT-IR) spectroscopy, UV-Visible, Raman spectroscopy, Fourier-transform nuclear magnetic resonance (FT-NMR) were used to gain insight of glass structure.

Chapter 4 presents results and discussion of as prepared samples. This chapter has been further sub-divided in two sections. **First section** describes the structural, mechanical, band gap and thermal properties of the prepared glass sealants to establish structure-properties correlation. Furthermore, hardness and indentation toughness of glasses are analyzed using the statistical aspect. The **second section** describes chemical compatibility of RO-B₂O₃-SiO₂-La₂O₃ [R = Mg, Ca, Sr, Ba] glass seals with Crofer 22APU metallic interconnect as a function of different heating durations of 5, 100 and 750 h to understand the mechanisms of interfacial interaction. The prepared diffusion couples were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), electron-probe microanalysis (EPMA) and X-ray dot mapping techniques. To gain insight into crystallization mechanism, various thermodynamic parameters like Lasocka parameter, activation energy of crystallization, frequency factor, crystallization constants and Avrami parameter have been evaluated using differential thermal analysis (DTA).

Chapter 5 presents study on the bonding and sealing behavior of RO-B₂O₃-SiO₂-La₂O₃ [R = Mg, Ca, Sr, Ba] glass seals and high temperature electrolyte (yttria-stabilized zirconia-YSZ) as well as intermediate temperature electrolyte i.e. titanium doped bismuth vanadate Bi₂V_{0.80}Ti_{0.2}O_{5.5-δ} (TBV) as function of different heating durations of 5, 100 and 750 h. Titanium doped bismuth vanadates (TBV) have been viewed as promising electrolyte conductor for low to intermediate temperature solid oxide fuel cells (IT-SOFC). The phase transition behavior, thermal analysis, expansivity and conductive behavior have been studied for Bi₂V_{1-x}Ti_xO_{5.5-δ} (0.05 ≤ x ≤ 0.20) in order to obtain the best conducting sample with desirable CTE. TBV have shown good conductivity along with thermal stability at 800 °C.

Chapter 6 concludes the results obtained from structural, thermal, optical and interaction study of glass/glass ceramics with Crofer 22APU/YSZ/TBV. At the end, future scope to enrich the study is also presented.

CHAPTER 1

INTRODUCTION

Overview

Lot of research is being carried out all over the world to commercialize the solid oxide fuel cell (SOFC) due to its ability to convert hydrocarbon fuels into electricity with higher efficiency. In this chapter, the description of these fuel cells has been given along with their comparative study. In addition to this, the role of sealants for planar SOFC stacks has been discussed. Rigid seals like glass and glass ceramics particularly containing alkaline earth elements are the most preferred sealant materials as they can sustain in stringent operating conditions of SOFCs. Hence, glasses, their processing conditions and effect of its components on various properties has been discussed. The present section also summarizes the interfacial interaction among glass seals and various components of SOFC.

1.1 Fuel cells and its types

Fuel cells have emerged as tantalizing alternatives as they have the potential to reduce the environmental impact and geopolitical consequences of the use of fossil fuels [1]. Like a combustion engine, a fuel cell uses some sort of chemical fuel as an energy source; but like a battery, the chemical energy is directly converted to electrical energy, without any inefficient combustion step [2-3]. Fuel cells are attractive for their modular and distributed nature, high efficiency, low emissions and zero noise pollution. The basic physical structure or building block of a fuel cell consists of an electrolyte layer in contact with a porous anode and cathode on either side. Together, these three are often referred to as the membrane-electrode assembly (MEA), or simply a single-cell fuel cell [4]. A schematic representation of a fuel cell with the reactant/product gases and the ion conduction flow directions through the cell is shown in fig. 1.1.

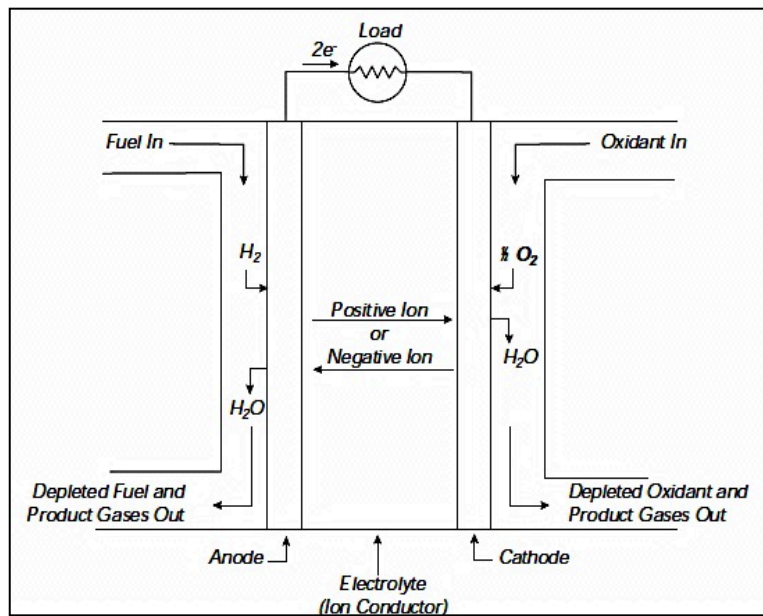


Figure 1.1: Schematic representation of individual fuel cell [4].

In the simplest example, a fuel such as hydrogen is brought into the anode compartment and an oxidant, typically oxygen, into the cathode compartment. There is an overall chemical driving force for the oxygen and the hydrogen to react to produce water. Direct chemical combustion is prevented by the electrolyte that separates the fuel (H_2) from the oxidant (O_2). The electrolyte serves as a barrier to gas diffusion, but will let ions migrate across it. A variety of fuel cells are in different stages of development. They can be classified by use of diverse categories depending on the type of electrolyte, operating temperature, efficiency and qualified power and

Table 1.1: Diverse categories of fuel cells depending on the type of electrolyte, operating temperature, efficiency and qualified power [5].

Fuel cell name	Electrolyte	Qualified power (W)	Working temperature (°C)	Efficiency (cell)	Efficiency (system)
Direct carbon fuel cell	Different types		700-850	80%	70%
Magnesium-Air Fuel Cell	salt water		-20 - 55	90%	
Microbial fuel cell	Polymer membrane or humic acid		< 40		
Regenerative fuel cell	Polymer membrane (ionomer)		< 50		
Proton exchange membrane fuel cell	Polymer membrane (ionomer)	100 W – 500 kW	50–120 (Nafion) 125–220 (PBI)	50–70%	30–50%
Reformed methanol fuel cell	Polymer membrane (ionomer)	5 W – 100 kW	250–300 (Reformer) 125–200 (PBI)	50–60%	25–40%
Direct-ethanol fuel cell	Polymer membrane (ionomer)	< 140 mW/cm ²	> 25 90–120		
Direct methanol fuel cell	Polymer membrane (ionomer)	100 mW ⁻¹ kW	90–120	20–30%	10–20%
Direct formic acid fuel cell (DFAFC)	Polymer membrane (ionomer)	< 50 W	< 40		
Planar Solid oxide fuel cell	O ²⁻ -conducting ceramic oxide	< 100 MW	500-1100	60–65%	55–60%
Tubular solid oxide fuel cell (TSOFC)	O ²⁻ -conducting ceramic oxide	< 100 MW	850-1100	60–65%	55–60%
Phosphoric acid fuel cell	Molten phosphoric acid (H ₃ PO ₄)	< 10 MW	150-200	55%	40% Co-Gen: 90%
Molten carbonate fuel cell	Molten alkaline carbonate	100 MW	600-650	55%	47%
RFC - Redox	Liquid electrolytes with redox shuttle and polymer membrane (Ionomer)	1 kW – 10 MW			
Protonic ceramic fuel cell	H ⁺ -conducting ceramic oxide		700		
Direct borohydride fuel cell	Aqueous alkaline solution		70		
Alkaline fuel cell	Aqueous alkaline solution	10 – 100 kW	< 80	60–70%	62%
Metal hydride fuel cell	Aqueous alkaline solution		> -20 (50% P _{peak} @ 0°C)		
Electro-galvanic fuel cell	Aqueous alkaline solution		< 40		
Enzymatic Biofuel Cells	Any that will not denature the enzyme		< 40		
Upflow microbial fuel cell (UMFC)			< 40		
Ring type fuel cell	O ²⁻ -conducting ceramic oxide	< 100MW	800-1100	60-70%	50-60%

are listed in table 1.1. The most common classification of fuel cells is by the type of material fabrication and includes (a) proton exchange membrane (polymer) electrolyte fuel cell (PEFC)

(b) alkaline fuel cell (AFC) (c) phosphoric acid fuel cell (PAFC) (d) molten carbonate fuel cell (MCFC) and (e) solid oxide fuel cell (SOFC). The schematic representation indicating their working temperatures, half-cell reactions and transporting ions are shown in fig. 1.2.

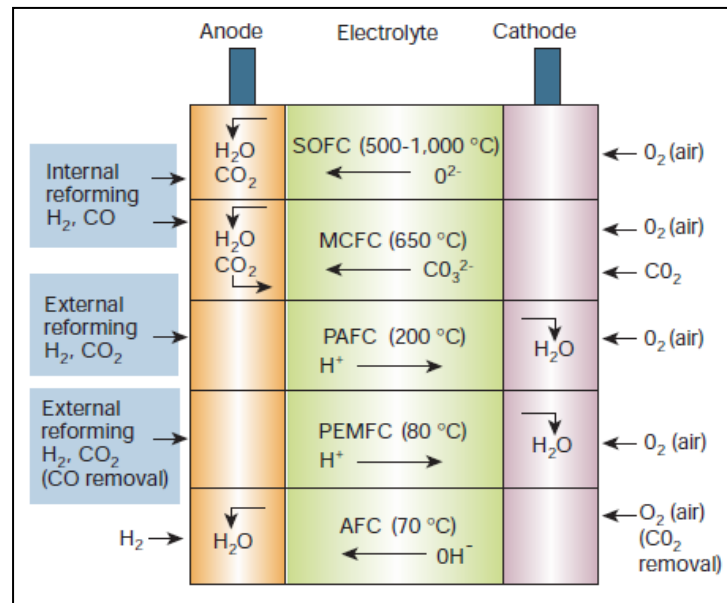


Figure 1.2: Fuel cells on the basis of reaction kinetics and transporting ions [2].

In low-temperature fuel cells (PEFC, AFC, PAFC), protons or hydroxyl ions are the major charge carriers in the electrolyte, whereas in the high-temperature fuel cells (MCFC and SOFC), carbonate ions and oxygen ions are the charge carriers, respectively [5-6]. The operating temperature and materials used in the cell components i.e. electrodes, electrolyte, and interconnect etc. determine the physicochemical and thermo mechanical properties of fuel cell. A three-phase interface is established among the reactants, electrolyte, and catalyst in the region of the porous electrode. The nature of this interface plays a critical role in the electrochemical performance of a fuel cell, particularly in those fuel cells with liquid electrolytes [7-8]. Aqueous electrolytes are limited to temperatures of about 200 °C or lower because of their high water vapor pressure and/or rapid degradation at higher temperatures. Even though the electrolyte has become the predominant means of specifying a cell, another important distinction is the method used to produce hydrogen for the cell reaction. Hydrogen can be reformed from natural gas and steam in the presence of a catalyst starting at a temperature of ~760 °C. The reaction is endothermic. MCFC and SOFC operating temperatures are high enough so that the reforming process can occur within the cell, a process referred to as internal reforming. The slow rate of the reforming reaction makes internal reforming impractical in the lower temperature cells.

Instead, a separate external reformer is used. Fuel processing and reforming process for the cells is demonstrated in figure 1.3. The operating temperature also plays an important role in dictating the type of fuel that can be utilized in a fuel cell. In high-temperature fuel cells, CO and CH₄ can be used because of the inherently rapid electrode kinetics and the lesser need for high catalytic activity at higher temperatures. Higher temperature cells also favor the conversion of CO and CH₄ to hydrogen and then use the equivalent hydrogen as the actual fuel.

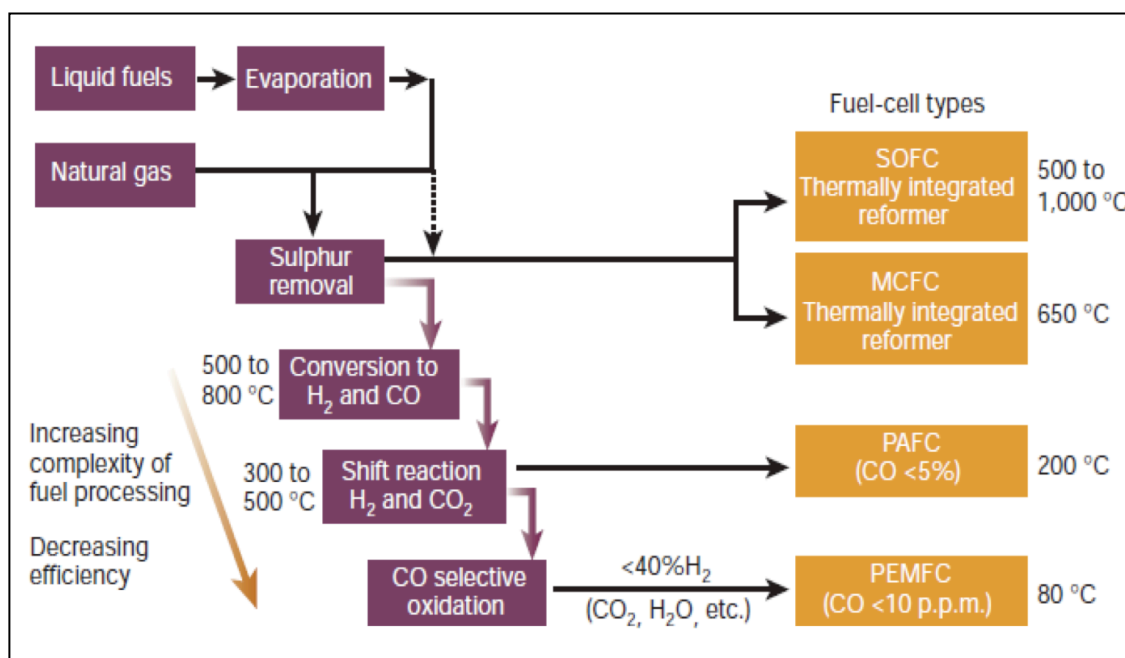


Figure 1.3: Fuel cell processing and reformation [2].

1.2 Solid oxide fuel cell (SOFC)

SOFCs have grown in recognition as a viable high temperature fuel cell technology. The SOFC is a complete solid-state device that uses an oxygen ion-conducting ceramic material as the electrolyte. There is no liquid electrolyte with its attendant material corrosion. Hence, electrolyte management issues that arise with the PAFC and MCFC do not occur with SOFC. Furthermore, the solid-state character of all SOFC components means no restriction on the cell configuration. It is therefore simpler in concept than all the other fuel cell systems described because only two phases (gas and solid) are required. The operating temperature of > 600 °C allows internal reforming, promotes rapid kinetics and produces high quality byproduct heat in cogeneration [9-11]. The high operating temperatures also mean that precious metal electrocatalysts are not needed. Both hydrogen and carbon monoxide can act as fuels in the SOFC. The operating principle of SOFC is very simple as depicted in fig. 1.4. Hence the

oxygen atoms are reduced on the porous cathode surface by electrons. The oxide ions diffuse through the electrolyte to the fuel rich porous anode, where they react with the fuel (hydrogen) and give off electrons to an external circuit.

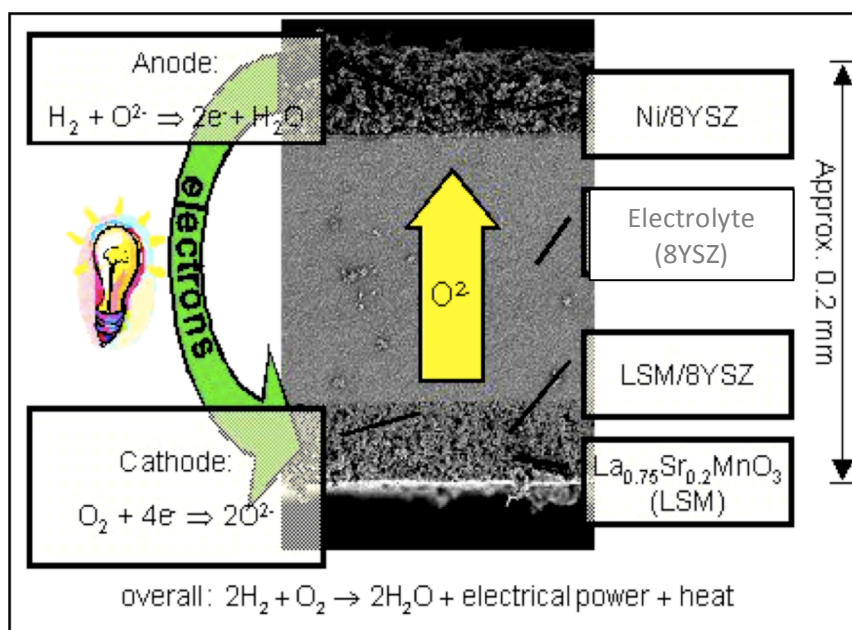


Figure 1.4: Schematic diagram of an individual fuel cell [1].

Thus, product water vapor is formed at the anode. A large amount of heat is produced by the electrochemical reaction, which can be used by an integrated heat management system. This fuel cell type, thus, addresses all the problems and takes full advantage of the inherent simplicity of the fuel cell concept.

1.3 Components of solid oxide fuel cells

The cell stack and components of SOFC are exposed to relatively high temperatures and a complex gas environment [1-9]. Components must be economic and resistant to microstructural changes, interfacial reactions, catalytic poisoning and corrosion. The detailed description of materials required for SOFC fabrication is given below:

1.3.1 Electrodes

The electrodes possess the following properties to ensure a smooth operation of the fuel cell:

- High electrical conductivity
- High surface area and catalytic activity

- Compatibility with other components of SOFC i.e. matching coefficient of thermal expansion (CTE).
- Porous surface in order to facilitate transport of gases.

For many years, platinum was the most common and only material that was used as electrode. It is economically not viable to build fuel cells with platinum electrodes. Hence the need to find low cost electrode materials such as perovskites (e.g. LaCoO_3 and LaMnO_3) are being investigated.

1.3.1.1 Anode: The oxidation reaction takes place at anode as demonstrated in fig. 1.5(a). The anode should have high porosity (20–40%) so that mass transport of reactant and product gases is not inhibited. The anode of state-of-the-art SOFCs is a cermet made of metallic nickel and YSZ skeleton. Nickel is used as anode because it is economical and exhibits high performance, although due to reasons of adherence and different expansion coefficients, it flakes off easily from the electrolyte unless it is mixed with zirconia, creating a cermet [12-15]. Ni-YSZ anode allows a rapid and clean connection with the fuel and is a good electronic conductor although Ni is susceptible to become coated with a carbon layer when it is reacting with carbon based fuels, which could prevent further reaction.

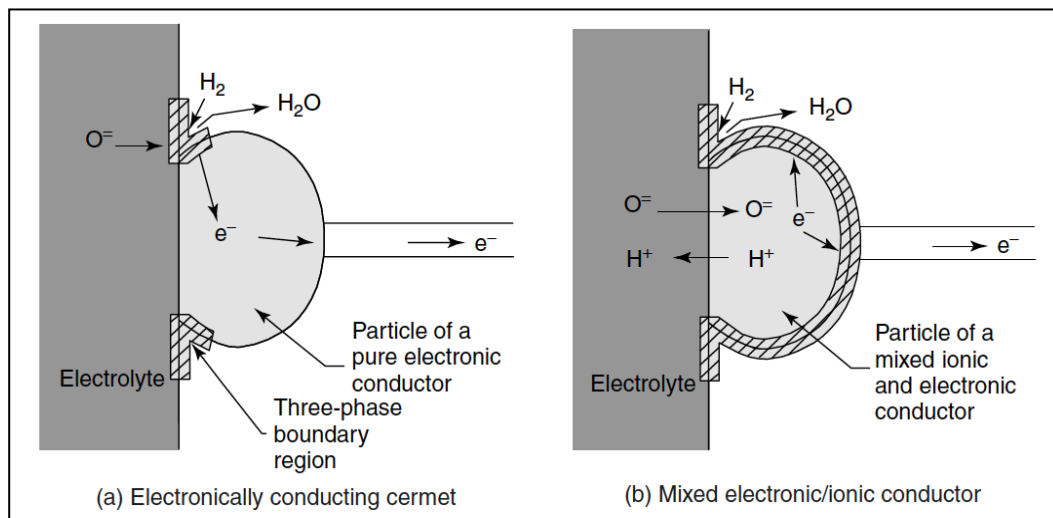


Figure 1.5: Illustration of three-phase boundary of different SOFC anode materials [12].

Certain additives to the Ni+YSZ cermet, such as 5% ceria or 1% molybdenum inhibit this process. Besides catalyzing the oxidation of hydrogen, Ni is also active in reforming of carbon containing fuels. Control of the particle size of the YSZ can also improve the stability of the anode under redox conditions. Most recently the attention of the developers has been directed

towards novel ceramic anodes that especially promote the direct oxidation of methane. Examples are Gd-doped ceria mixed with Zr and Y, and various TiO_2 -based systems. In such anodes, there is mixed conductivity for both electrons and oxygen ions. Further advantage of using mixed conductors as anodes is that they can provide a means of extending the three-phase boundary between reactant-anode electrolyte, as shown in fig. 1.6(a).

1.3.1.2 Cathode: The cathode material is very important since cathodes operate in a highly oxidizing environment as shown in fig. 1.6(b) unlike anode material (fig. 1.6(a)). Similar to the anode, the cathode is a porous structure that must allow rapid mass transport of reactant and product gases. Although adequate for most SOFCs, other materials may be used, particularly attractive being p-type conducting perovskite structures that exhibit mixed ionic and electronic conductivity. The best materials are semiconducting oxides, such as doped lanthanum cobaltites and lanthanum manganites. Strontium-doped lanthanum manganite ($\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$), a p-type semiconductor, is most commonly used for the cathode material [16-18]. A new material $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) has the suitable properties i.e. good electronic conductivity and matching expansion coefficient.

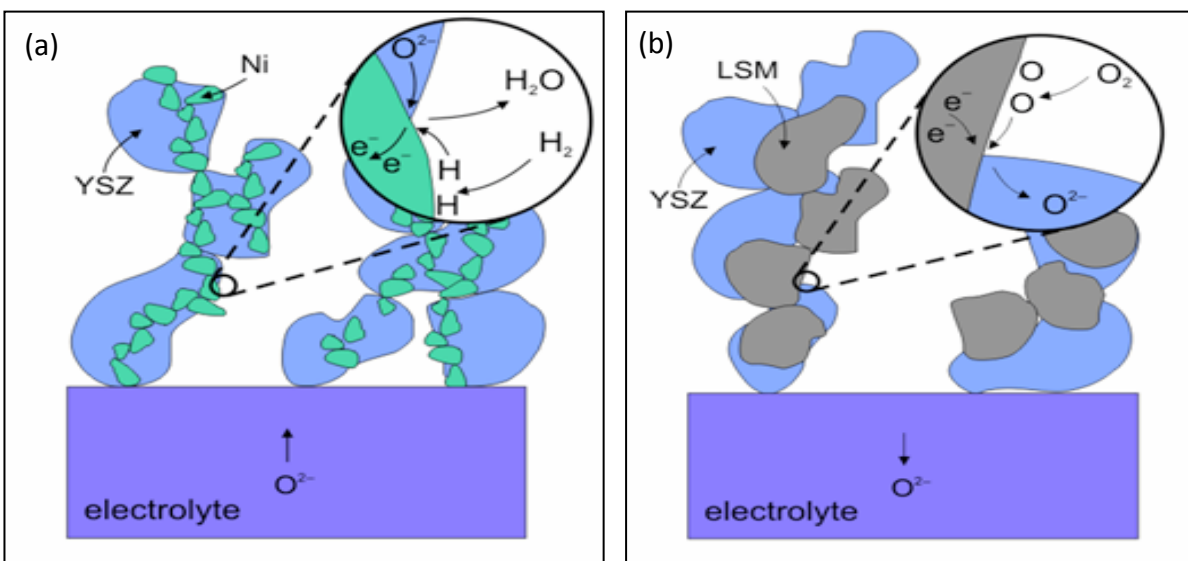


Figure 1.6: (a) Oxidation reaction on the surface of an anode made of Ni-YSZ (b) Reduction reaction on the surface of a cathode made of LSM-YSZ (Image courtesy of Risø National Laboratory).

Other materials have also been used, such as $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF). LSCF has the advantage of lower power losses at lower temperatures and less susceptibility to poisoning by chromium and it is used with ceria-based electrolytes. This is especially important for lower-

temperature operation since the polarization of the cathode increases significantly as the SOFC temperature is lowered. For cells operating at around 650 °C, the advantages of using mixed conducting oxides become apparent. The perovskites, lanthanum strontium ferrite, lanthanum strontium cobalite, and n-type semiconductors are better electrocatalysts than lanthanum strontium manganite, because they are mixed conductors. The performance decay of cathode is mainly due to changes in the microstructure and the phase composition of the material at load conditions. If stainless steel interconnects are used, degradation is caused by Cr poisoning, since it evaporates from the steel and condensates preferably on the cathode. In general, the rate Cr poisoning decreases with decreasing operating temperature.

1.3.2 Electrolytes

Good electrolyte should have crystal structures with open channels, layers to provide pathways for easy ionic transport via hopping mechanism. There are several criteria, which should be fulfilled by electrolyte. The electrolyte should be:

- Dense and leak tight.
- Stable in reducing and oxidizing environments.
- Good ionic conductor at operating temperatures.
- Non-electron conductor.
- Thin to reduce ionic resistance and extended in area for maximum current capacity.
- Thermal shock resistant and economical.

For high temperature SOFC (800-1000 °C), there are two main groups of such ion conductors: fluorite structured and perovskite structured materials. Besides these new materials, third category of materials has also been investigated by the researchers i.e. hexagonal structured oxides. For low-intermediate temperature SOFC (600-800 °C), aurivillius and brownmillerite structures are preferred. The three most common electrolyte materials are: yttria stabilized zirconia (YSZ), doped ceria (CeO_2), doped lanthanum gallate (LaGaO_3 - oxygen ion conductors) and doped barium zirconate (BaZrO_3 - a proton conductor) [19-22]. The concentration and type of the dopants influence the material properties strongly. Dopants, that cause the least strain and hence the least influence on the potential energy of the parent lattice, have the biggest effect on the conductivity. The present investigation focuses on high temperature YSZ and intermediate temperature doped bismuth vanadates.

1.3.2.1 High temperature YSZ electrolyte: Fluorite oxides are the most common and classical oxygen ion conducting materials for high temperature-SOFC. The crystal structure consists of a cubic oxygen lattice with alternate body centers occupied by eight coordinated cations. The cations are arranged into a face centred cubic structure with the anions occupying the tetrahedral sites. This leaves rather an open structure with large octahedral interstitial void. Yttria-stabilized zirconia (YSZ) is still the most effective electrolyte for the HT-SOFC. Zirconia is highly stable in both the reducing and oxidizing environments that are to be found at the anode and cathode of the fuel cell, respectively. The ability to conduct O^{2-} ions is brought about by the fluorite crystal structure of zirconia in which some of the Zr^{4+} ions are replaced with Y^{3+} ions. When this ion exchange occurs, a number of oxide-ion sites become vacant because of three O^{2-} ions replacing four O^{2-} ions. Oxide-ion transport occurs between vacancies located at tetrahedral sites in the perovskite lattice, and the process is now well understood at the atomic and molecular level. The ionic conductivity of YSZ (0.02 S cm^{-1} at 800°C and 0.1 S cm^{-1} at 1000°C) is comparable with that of liquid electrolytes [21-22]. For YSZ electrolyte, current flows by the movement of oxide ions through the crystal lattice as shown in fig. 1.7.

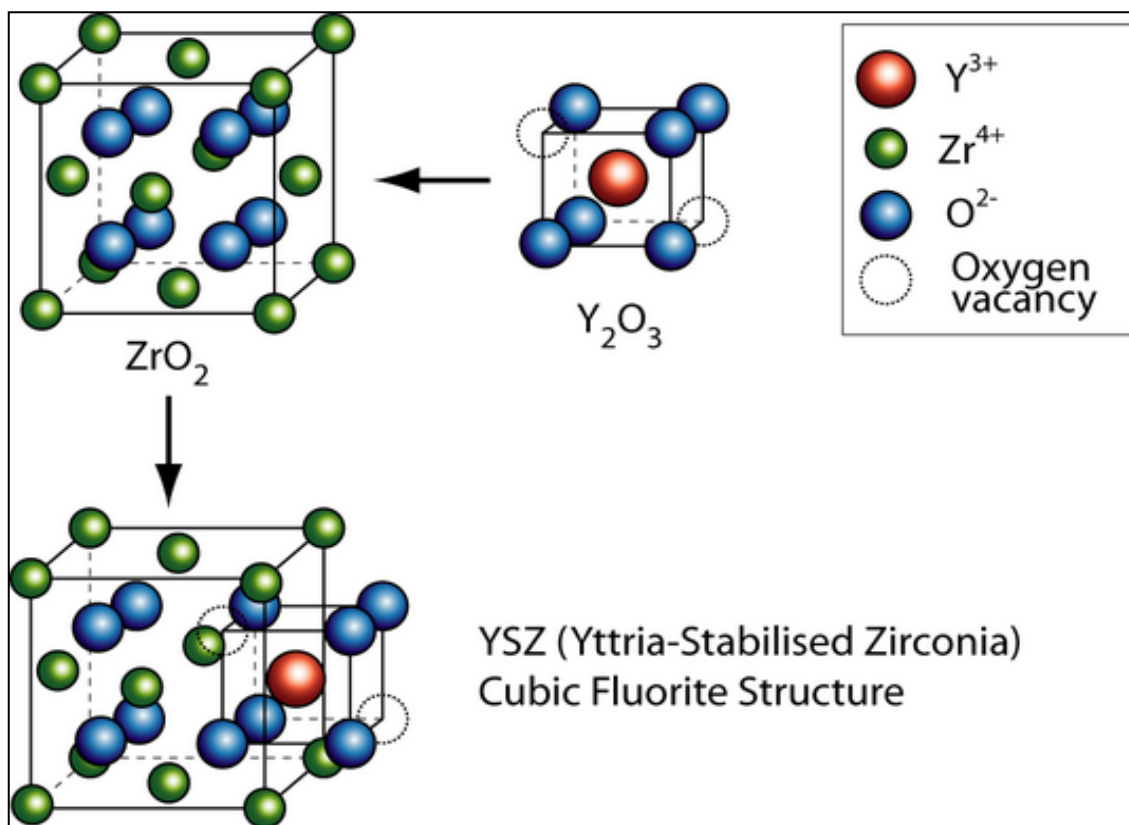
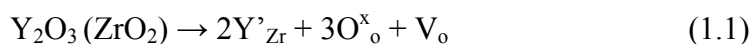


Figure 1.7: Vacancy transport in YSZ [19].

It is a thermally activated process, where the ions hop from one lattice site to the other (from one potential valley to the other) in a random way. When an electric field is applied, there is a drift in one direction superimposed on the random thermal motion. Zirconia in its pure form has high melting temperature and a low thermal conductivity. The applications of pure zirconia are restricted because it shows polymorphism. It is monoclinic at room temperature and changes to the denser tetragonal phase at 1000 °C. This transformation involves a large change in the volume and causes extensive stress in crystal lattice. Hence zirconia has a low thermal shock resistivity. The addition of some oxides results in stabilizing the cubic phase and the creation of one oxygen vacancy i.e.



For electrolytes, high strength and toughness are also desirable in addition to high ionic conductivity especially for its applications in solid oxide fuel cell. The bending strengths of zirconia-based electrolytes along with their CTE are also shown in table 1.2.

Table 1.2: Zirconia based electrolytes with their bending strength and thermal expansion [23].

Electrolyte	Conductivity at 1000 °C (S cm ⁻¹)	Bending strength (MPa)	CTE × 10 ⁻⁶ /°C
ZrO ₂ - 3 mol% Y ₂ O ₃	0.059	1200	10.8
ZrO ₂ - 8 mol% Y ₂ O ₃	0.13	230	10.5
ZrO ₂ - 9 mol% Y ₂ O ₃	0.13	-	-

1.3.2.2 Intermediate temperature BIMEVOX electrolytes: For IT-SOFC, the metal ion doped bismuth vanadates (BIMEVOXes) are a group of fast oxygen ion conducting solid electrolytes based on cation substitution for vanadium in the parent compound Bi₄V₂O_{11-δ}. They possess excellent ionic conductivities, particularly at low and intermediate temperatures, which can be in the range of 10⁻³ S cm⁻¹ at 300 °C and 10⁻¹ S cm⁻¹ at 600 °C. Bi₂VO_{5.5-δ} consists of alternate bismuth-oxygen (Bi-O) and vanadium oxygen (V-O) layers. Bi-O layer in [Bi₂O₂]²⁺ exhibits square pyramidal co-ordination for bismuth as shown in fig. 1.8. Stereochemical activity of non-bonding 6s² lone pairs of Bi contributes for its asymmetric coordination geometry. Electroneutrality of the system is preserved by VO₆ octahedrons present in V-O layer [VO_{3.5}] [24-25]. Bi₂VO_{5.5-δ} exhibit three different structures in temperature range from room temperature to 900°C whose crystalline structures are explained using subcell of a_m = 0.55, b_m =

0.56 and $c_m = 1.53$ nm [26-28]. At low temperature (< 445 °C) monoclinic α phase is reported, which is generally n-type semiconductor having unit cell volume of $3a_m \times b_m \times c_m$. At intermediate temperature (445 °C – 570 °C) orthorhombic β phase, which is oxygen ion conductor having unit cell volume of $2a_m \times b_m \times c_m$ is formed whereas at high-temperature (≈ 700 °C) tetragonal γ phase is observed, which is an oxygen ion conductor having volume of $(a_m/\sqrt{2}) \times (a_m/\sqrt{2}) \times c_m$.

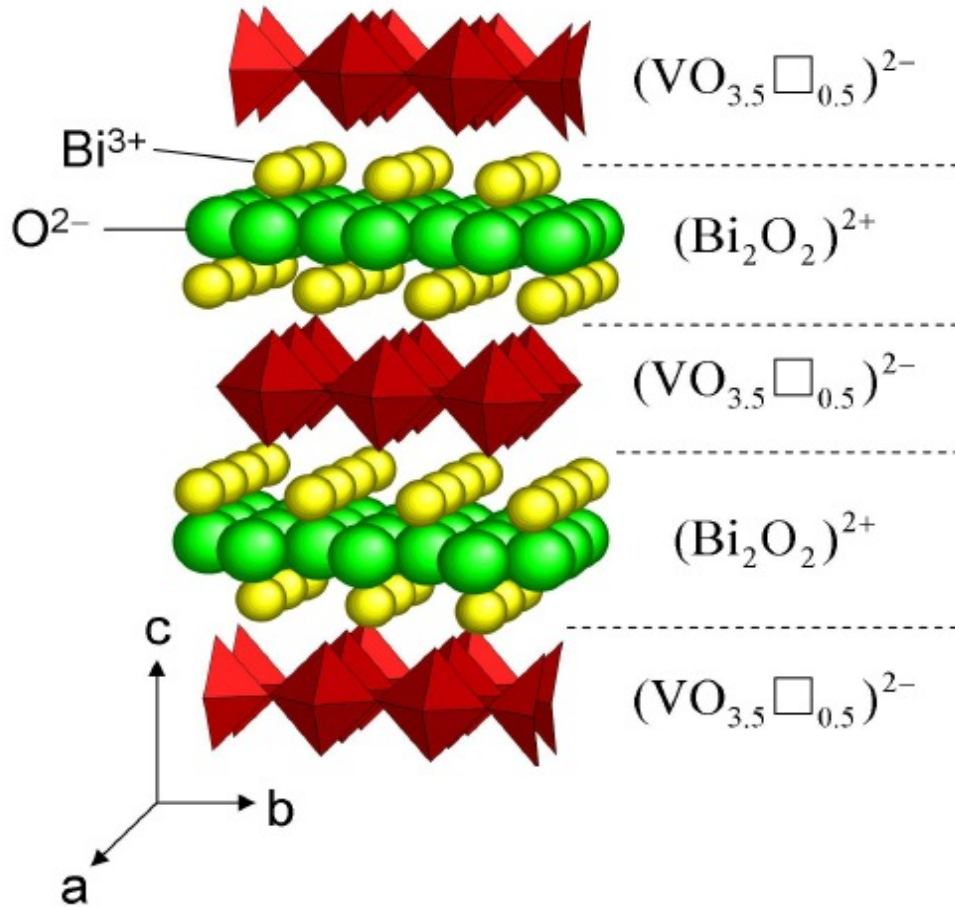


Figure 1.8: Single layer Aurivillius structure [28].

Figure 1.9 demonstrates the structural arrangement of all phases. The three phases show similar profiles except for split peaks such as (2 2 0) at about 46° and characteristic superlattice diffraction peaks (e.g., $1/3$ 1 3 at about 24° for α phase, $2/3$ 1 3 at about 26° for the β phase). In the γ phase, some diffraction peaks, e.g., (0 2 0) and (2 0 0) at about 32° merge and no superlattice diffraction peaks are observed. α phase is an n-type semiconductor. Meanwhile, β phase exhibits the oxide-ion conductivity as high as 10^{-2} S cm⁻¹ at 500 °C, and γ -Bi₂VO_{5.5-δ}

exhibit the oxide-ion conductivity $6 \times 10^{-1} \text{ S cm}^{-1}$ at 700°C . Figure 1.10 demonstrates conductivity behavior for some selected bismuth vanadate samples.

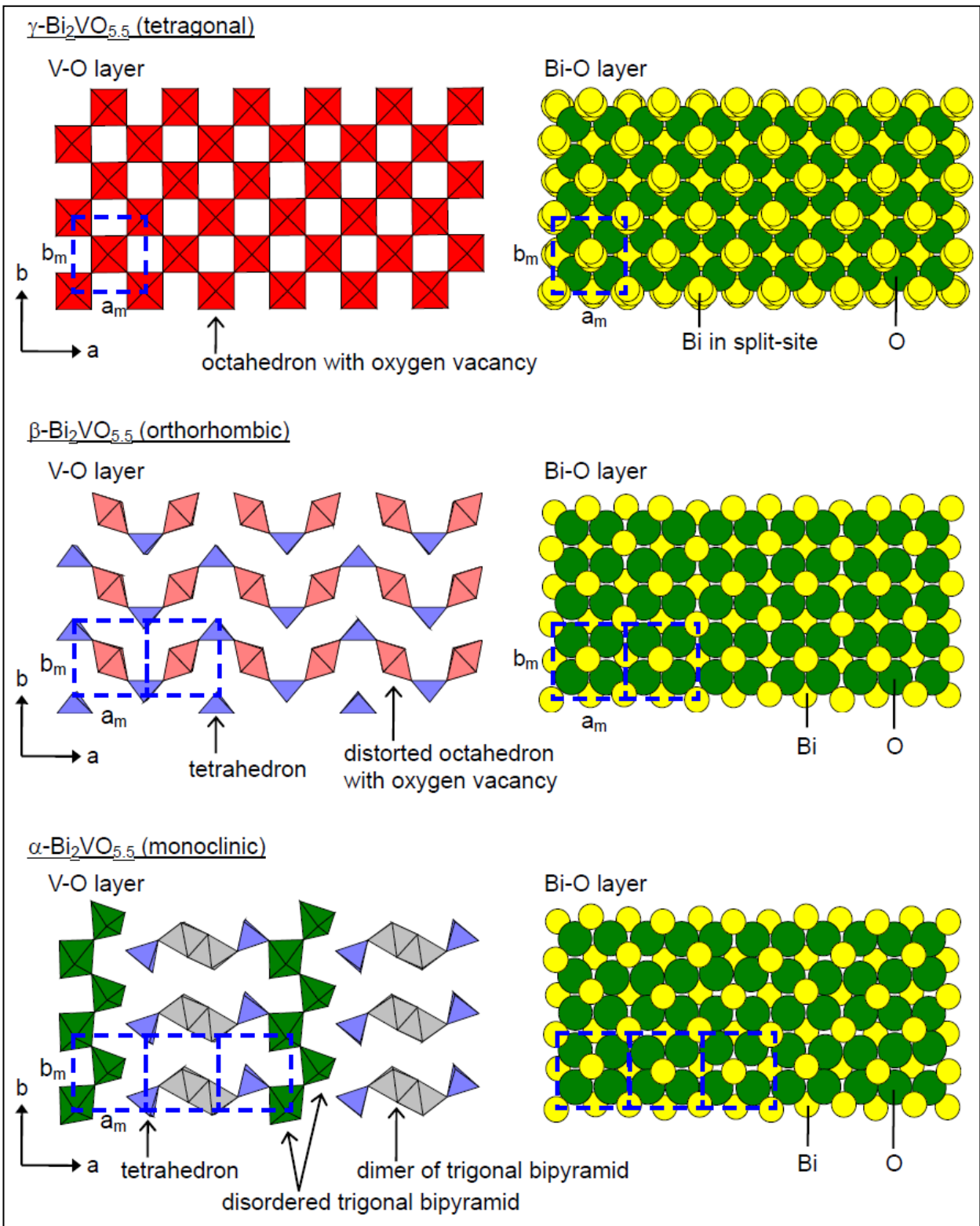


Figure 1.9: Structural arrangement of all possible bismuth vanadate phases [29].

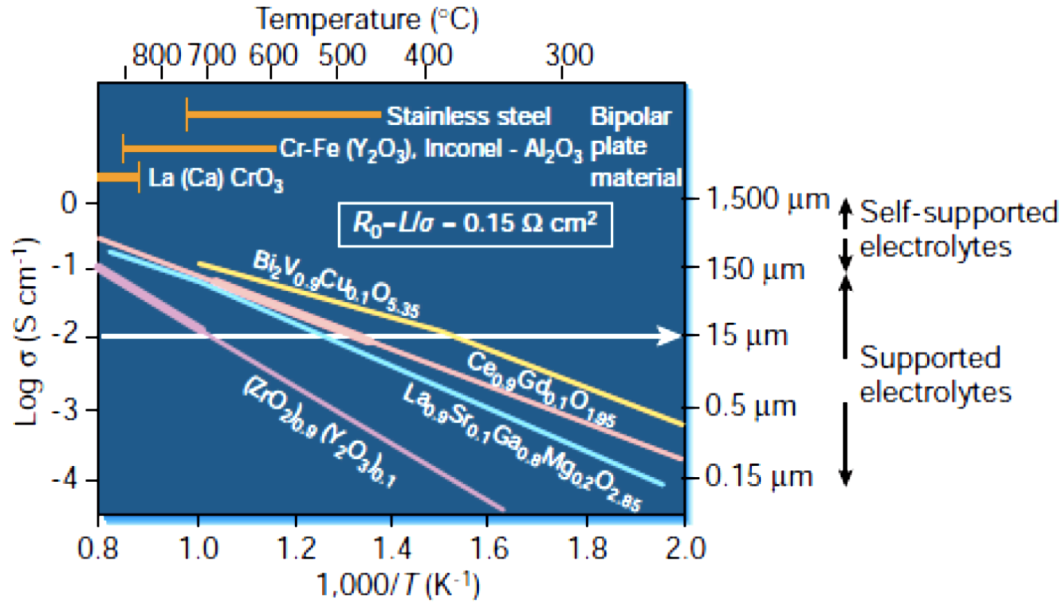


Figure 1.10: Conductivity behavior of selected electrolytes for SOFC [2].

1.3.3 Interconnect (Separator)

The ‘interconnect’ is the means by which connection is achieved between neighboring fuel cells. In planar fuel cell terminology this is the bipolar plate, but the arrangement is different for tubular geometries as described in the next section. For the interconnection, an inert and impervious material is needed. It should withstand both oxidizing and reducing environments. Lanthanum chromite seems to have the necessary properties in systems operating at 1000 °C. Depending on doping, this material matches the CTE of LSM [1-10]. For lower temperatures, metallic based alloys can be used. Plasma spraying is the most economic method of applying the interconnect layer on the electrode. Although lanthanum provides cell life of up to 70000 h, it is not perfectly inert and it expands in the presence of hydrogen, causing cracking especially at large planar stacks. Metals can be used as interconnect, but these tend to be expensive. Crofer 22APU is the commercialized interconnect for SOFC having CTE of $11.8 \times 10^{-6} / ^\circ\text{C}$. Conventional steels also have a mismatch in CTE with the YSZ electrolyte. To overcome this, Siemens and others have tried to develop new alloys, such as the Cr-5Fe-1Y₂O₃ Siemens/Plansee alloy. Unfortunately, such alloys can poison the cathode with chromium. Under the cathode atmosphere, chromium can evaporate from the interconnect and deposit at the (La,Sr)MnO₃ (LSM)/YSZ/gas three-phase boundary resulting in rapid deactivation of the cathode.

1.4 Configuration of SOFC

Like other cells, it is necessary to stack SOFCs to increase the voltage and power being produced. Because there are no liquid components, the SOFC can be cast into flexible shapes. As a result, the cell configurations can respond to other design prerequisites [12-14]. This feature has resulted in two major configurations and variations of them are described below.

1.4.1 Tubular configuration

The most developed solid oxide fuel cell is the Siemens Westinghouse tubular cell [30]. This approach results in eliminating seal problems between adjacent cells. A schematic representation of the cross section of the present Siemens Westinghouse tubular design is shown in figure 1.11 (a). Air is fed through a thin alumina air supply tube located centrally inside each tubular fuel cell. Heat generated within the cell brings the air up to the operating temperature.

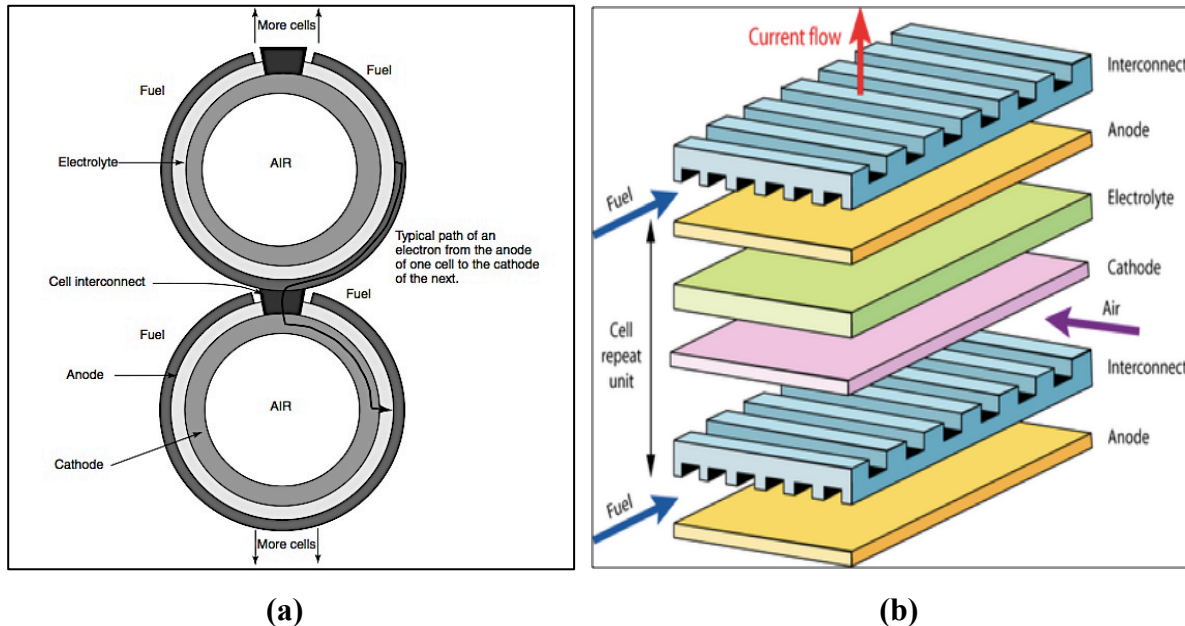


Figure 1.11: (a) Tubular design of SOFC (b) Exploded view of planar SOFC [12].

The air flows through the fuel cell back up to the open end. At this point air and unused fuel from the anode exhaust mix are instantly combusted so that the cell exit attains the temperature above 1000 °C. One attractive feature of this arrangement is that it eliminates the need for leak-free gas manifolding of the fuel and oxidant streams. However, the seal less tubular design results in a relatively long current path around the circumference of the cell to the interconnect, limiting performance resulting in lower power density.

1.4.2 Planar configuration

The planar design offers 1) high power density, 2) structural ruggedness, 3) concealed electrodes, 4) ease of heat removal, and 5) low-stress assembly relative to the tubular design. Solid electrolyte structures of YSZ up to 10 cm diameter and 0.25 mm thickness with better than 0.025 mm flatness have been fabricated for this design. The interconnect, having ribs on both sides, forms gas flow channels and serves as a bipolar gas separator contacting the anode and cathode of adjoining cells as shown in fig. 1.11 (b). Fuel and oxygen flow occurs perpendicular to each other via the ribs in interconnect. However, one of the technological problems in the development of planar-SOFC is the requirement of high temperature gas tight seals at the edges of the plates (fig. 1.12). In a SOFC, the purpose of sealing is to prevent the mixing of air and fuel gasses (H_2 , CO_2 , CH_4) during operation [31-34].

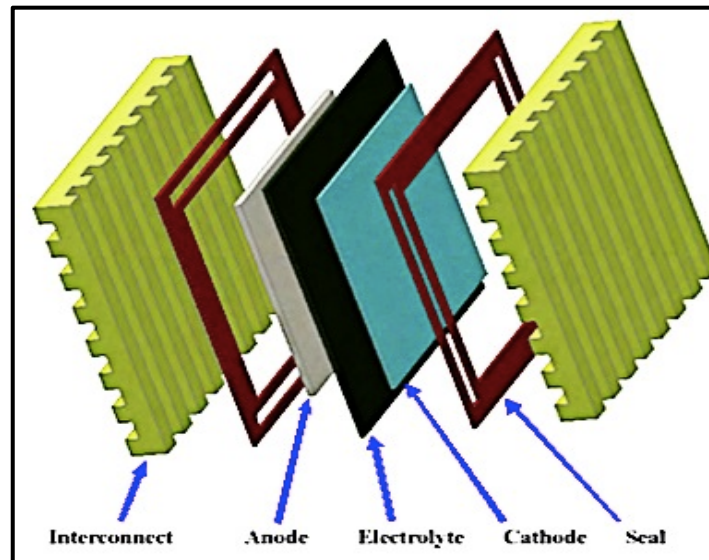


Figure 1.12: Seal and cell interconnection [35].

Leakage of fuel into air will lead to direct combustion and may cause local overheating with decreased efficiency. In order to achieve long-term uninterrupted performance of SOFC stack, an appropriate sealing material for pSOFC is required.

1.5 Sealing materials and their types

Table 1.13 illustrates all the fundamental properties, which must be satisfied by a sealant to ensure uninterrupted operation of SOFC [12-19]. Typical conditions under which SOFC operate and hence seals will be exposed include:

- An average operating temperature of 800 -1000 °C.

- Continuous exposure to an oxidizing atmosphere on the cathode side and a wet reducing gas on the anode side.
- An anticipated lifetime of the device should be more than 10000 hours.
- Under thermal stresses due to mismatch of CTE.

Therefore, the selection of sealing materials/techniques is closely tied to the specific application in which the stack will be used. Thus, it is dependent on a number of design factors, including individual cell and stack materials and geometries, stack assembly sequence, thermal gradients expected across the seal and other stack components, maximum weight and/or volume of the power plant, anticipated external forces, and required heating and/or cooling rate of the device. Concepts of sealing which are developed for fabricating seals have been described below.

Table 1.3: Requirements of a hermetic sealant [36].

<u>Mechanical</u>	<u>Design/Fabrication</u>
Hermetic Sealing or Marginal, Non-Localized Leak Rate	Low cost
CTE Matching or Mitigation of CTE Mismatch Stresses	Facile application/processing
Acceptable Bond Strength or Compressive Loading Requirement (i.e., Load Frame Design)	High reliability with respect to achieving initial hermeticity (seal conforms to non-flat substrate surfaces)
Resistant to Degradation Due to Thermal Cycling/Thermal Shock	Acceptable sealing environment/temperature (i.e., has little effect on the subsequent performance of the stack)
Robust under External Static and Dynamic Forces*	Design flexibility (e.g., allows use of Ni-based alloys in the interconnect)*
<u>Chemical</u>	<u>Electrical</u>
Long-Term Chemical Stability under Simultaneous Oxidizing/Wet Fuel Environments	Non-conductive (non-shorting configuration)*
Long-Term Chemical Compatibility with the Adjacent Sealing Surfaces	
Resistant to Hydrogen Embrittlement	

1.5.1 Compressive seals

Compressive seals employ deformable materials that do not bond to the pSOFC components but instead serve as gaskets. Thus, sealing results when the entire stack is compressively loaded. Because the sealing material conforms to the adjacent surfaces and is under constant compression during use, it forms a dynamic seal [37-38]. That is, the sealing surfaces can slide past one another without a disruption in hermeticity and the individual stack components are free to expand and contract during thermal cycling with no need to consider CTE matching.

This offers stack designers greater freedom in utilizing alloys other than ferritic stainless steels for the metal components. However, to employ compressive seals in a pSOFC stack, a load frame is required to maintain the desired level of compression on the stack, which introduces several complexities in stack design. These factors increase system cost and limit the use of compressive seals in mobile applications.

1.5.2 Compliant bonded seals

The sealant used in compliant bonded sealing forms a joint that can be plastically deformed at or above room temperature. This mitigates the effects of CTE mismatch stresses to some degree and lessens the requirements of CTE matching between stack components [39-41]. However, there are still potential issues related to cell bowing and the accompanying non-uniformities in gas distribution. In addition, all of the sealing concepts in this category are metal-based and electrically conductive. Thus, they cannot be used as the sole sealing solution for a pSOFC stack design without introducing the need for insulating layers to prevent internal short-circuiting.

1.5.3 Brazing

One of the most reliable methods of joining dissimilar materials is brazing. In this technique, a filler metal between components is heated to a point at which it becomes molten and under capillary action fills the gap between the sealing surfaces. When the material gets cooled, a solid joint forms [42]. Unfortunately, active metal brazing is typically conducted in an inert or vacuum environment. In addition, it has been shown that the ceramic-metal joint produced by this technique is not sufficiently resistant to oxidation and will degrade under exposure of high temperature.

1.5.4 Rigid bonded seals / glass seals

In rigid bonded sealing, the sealant forms a joint that is non-deformable at room temperature. Majority of SOFC seal development has focused on bonded rigid seals primarily glass and glass-ceramics, which essentially “glue” the stack components together [36-40]. Two important criteria for selection of a suitable glass sealant are the glass transition temperature (T_g) and the CTE. T_g is characteristic temperature above, which the mechanical properties of the material change from brittle to elastic. 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 flow characteristics/ viscosity is described by softening temperature (T_s). CTE must match other cell components, such as electrolyte and the interconnect material to minimize thermal stresses during the SOFC operation. The composition of glass sealant can be tailored to match the CTE of the adjacent substrates. Hence, these materials are found to satisfy the following criteria:

- Stability in the reducing and oxidizing atmospheres of the stack.
- Electrically insulation (resistivity $> 2 \text{ k}\Omega \text{ cm}$).
- Readily applied to the sealing surfaces as a powder dispersed in a paste or a tape cast sheet.
- Typically exhibit good wetting behavior on both yttria-stabilized zirconia (YSZ) and stainless-steel surfaces.
- Can be engineered to exhibit a CTE matching those of the adjacent pSOFC components.

The requirements allow specific oxide components of a sealing glass-ceramic, which form a systematic pattern in the periodic table of the elements. Subsequent sections describe brief introduction to glasses and their applicability as sealants.

1.6 Glasses

Glass is an amorphous solid, without long-range order [43-44]. Glasses are typically brittle, and often optically transparent. Glasses and crystals have the same building blocks (cation polyhedra) arranged in a different pattern; e.g. glasses have broader distributions of bond angles.

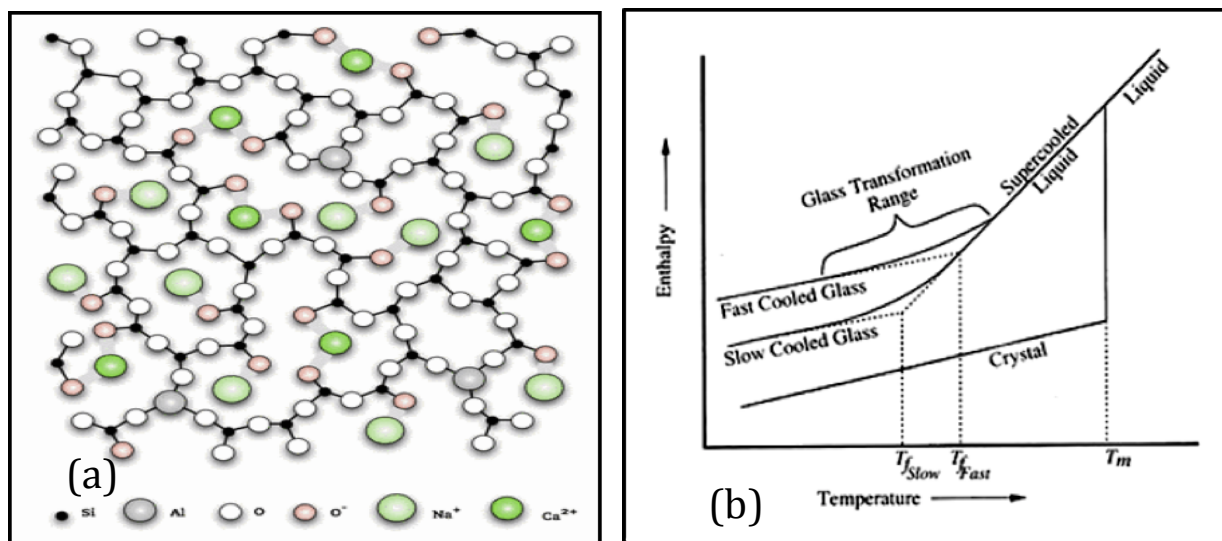


Figure 1.13: (a) Structure of glass and (b) Enthalpy- temperature diagram [44].

The atoms in glass are arranged in a random manner of that of a liquid because glass is essentially a super-stiff liquid as shown in Fig.1.13 (a). All glasses are found to share following characteristics [44]:

(a) Glass is a super cooled liquid, meaning that it is rigid and static i.e. the liquid continues to rearrange as the temperature decreases, but no abrupt change in enthalpy due to structural arrangements.

(b) Every glass exhibits time-dependent glass transformation behavior. This behavior occurs over a temperature range known as the glass transformation region. A glass can thus, be defined as “an amorphous solid completely lacking in long range periodic atomic structure and exhibiting a region of glass transformation behavior.”

As indicated by the enthalpy temperature diagram (fig. 1.13 (b)), the glass transformation occurs over a range of temperatures and cannot be characterized by any single temperature. The glass transformation temperature, or the glass transition temperature, (T_g), is rather vaguely defined by changes in either thermal analysis curves or thermal expansion curves. The values obtained from these two methods, while similar, are not identical. The values of temperature are obtained as a function of the heating rate used to produce these curves. However, T_g is a useful indicator of the approximate temperature where the super cooled liquid converts to a solid on cooling, or, conversely, of which the solid begins to behave as a visco-elastic solid on heating.

1.7 Glass components

In general, glasses are either produced from high quality chemically pure components or from a mixture of far less pure minerals. Regardless of the source of the components used to produce a specific glass, the batch materials can be divided into five categories on the basis of their role in the process [43-45]. These components are listed in table 1.4 and explained as follows:

1.7.1 Glass formers: The most essential component of any glass batch is always the glass former, which serves as the primary source of the structure. The cations, which form oxygen polyhedral triangles and tetrahedral for glass, are called glass network formers. The identity of these components usually serves as the basis for the generic name used for the glass. If a significant amount of boric oxide is present in addition to silica, then the sample is termed borosilicate glass. The glass former bond strength lies in the range 60-80 kcal/mol, low coordination number ($3 < CN < 4$) and high field strength (1-2).

Table 1.4: Some glass network formers, glass modifier and intermediate oxides with their properties [44].

Role of oxide	M in MO _x	Valence electrons	Dissociation Energy E _d per MO _x (kcal)	Coordination number	Single bond strength (kcal)
Glass former	B	3	356	3	119
	Si	4	424	4	106
	Ge	4	431	4	108
	Al	3	402-317	4	101-79
	B	3	356	4	89
	P	5	442	4	111-88
	V	5	449	4	112-90
	As	5	349	4	87-70
	Sb	5	339	4	85-68
	Zr	4	485	6	81
Intermediate	Ti	4	435	6	73
	Zn	2	144	2	72
	Pb	2	145	2	73
	Al	3	317-402	6	53-67
	Th	4	516	8	64
	Be	2	250	4	63
	Zr	4	485	8	61
	Cd	2	119	2	60
Modifier	La	3	406	7	58
	Y	3	399	8	50
	Sn	4	278	6	46
	Ga	3	267	6	45
	In	3	259	6	43
	Th	4	516	12	43
	Pb	4	232	6	39
	Mg	2	222	6	37
	Li	1	144	4	36
	Pb	2	145	4	36
	Zn	2	144	4	36
	Ba	2	260	8	33
	Ca	2	257	8	32
	Sr	2	256	8	32
	Cd	2	119	4	30
	Na	1	120	6	20
	K	1	15	9	13
	Rb	1	115	10	12
	Hg	2	68	6	11
	Cs	1	114	12	10

1.7.2 Glass modifiers: These ions take up random positions in the glass network and thus modify or change the structure of glass network by providing additional oxygen ions. These oxygens are known as non-bridging as they do not link polyhedral units. The network modifier bond strength usually lies in the range 10-40 kcal/mol, CN between 6 to 8 and low field strength (0.35). Alkaline earth elements are common modifiers that generally locate into cavities of the glass network.

1.7.3 Glass Intermediates: Some oxides can either work as a network former or network modifier, which depends on their chemical nature. The bond strength of these oxides usually lies in the range between 50 - 60 kcal/ mol, CN between 4 to 8 and field strength in the range 0.84- 1.04.

1.7.4 Colorants: Colorants are used to control the color of the final glass. In most cases, colorants are oxides of either the 3d transition metals or the 4f rare earth elements. Gold and silver are also used to produce colors by formation of colloids in glasses. Iron, copper and manganese ions also add color to glasses.

1.7.5 Fining agents: Fining agents are added to glass forming batches to promote the removal of bubbles from the melt. Fining agents include the arsenic and antimony oxides, potassium and sodium nitrates, NaCl, fluorides such as CaF_2 , NaF , and Na_3AlF_6 and a number of sulfates. These materials are usually present in very small quantities (<1 wt %).

1.8 Theories of glass formation

The first models of glass structures were centered on silicate crystals. The microcrystal approach suggested that glasses are simply masses of very small microcrystals. The small size of these crystals can be used to explain the lack of structure in X-ray diffraction pattern. Lebedev and others from Russia formed crystallite model, which is a different version of microcrystal approach. Their crystallites differ from microcrystals in that the structures are deformed versions and are not merely smaller sized versions of normal crystals. Glass was assumed to consist of crystallites connected by amorphous regions. This theory also assumed that the properties of glasses in a specific system are associated with phase diagram. Following structural models are the most common structural models, which address the formation of glass network [43-45].

1.8.1 Goldschmidt's criterion (1926)

The criterion proposed by Goldschmidt refers to the ratio of the ionic radii r_A/r_O of the cation and oxygen, for simple oxides with formula A_mO_n . This criterion implies a tetrahedral coordination. In fact to vitrify the oxides should have a ratio between 0.2 and 0.4 and, according to the considerations of crystal chemistry for ionic structures, this ratio is correlated to the coordination number of four for the central cation.

1.8.2 Zachariasen random network theory (1932)

The most commonly used models for glass structures are based on original ideas of Zachariasen. Certain polyhedra are more likely to form the disordered networks particular to a glass. Glasses have greater structural energies/amorphous structures. Zachariasen gave the following rules of glass formation: -

1. No oxygen atom may be linked to more than two cations.
2. The cation coordination number is small: 3 or 4.
3. Oxygen polyhedra share corners, not edges or faces.
4. For 3D networks, at least three corners must be shared.

In general, all four rules should be satisfied for glass formation to occur.

1.8.3 Dietzel theory (1942)

After Zachariasen, others scientists have applied the principles of crystal chemistry to define the role of oxides in the formation of a glass. In 1942, Dietzel suggested the measurement of the strength of a cation-oxygen bond as a parameter to determine the effect of cations on the behaviour of the glass. So it is possible to classify cations in oxide substances according to their field strength. This quantity is calculated through the ratio z/a^2 , where z is the valence of the cation and a is the distance between the cation and the oxygen. Dietzel examined direct Coulombic interactions:

$$\text{Attractive force} = [(z_c e)(z_a e)]/(r_c + r_a)^2 \quad (1.2)$$

Let $a = (r_c + r_a)$ and (for oxides) $z_a = -2$; then Dietzel categorized cations using:

$$\text{Field strength} = z_c/a^2 \quad (1.3)$$

High field strength implies high cation-oxygen bond energy. Glass formers have field strength >1.3 whereas glass modifiers possess field strength <0.4 . The field strength of intermediates lies between (0.4-1.3).

1.8.4 Sun theory (1947)

Sun considered a single bond strength (SBS) approach. Dissociation energy (E_d) for a molecule is given by:



For single bond it is $\sim E_d/\text{Coordination number}$. Sun noted that:

- High SBS oxides (>80 kcal/bond) $\rightarrow$ glass formers
- Low SBS oxides (<60 kcal/bond) $\rightarrow$ glass modifiers
- Intermediate SBS oxides (60-80 kcal/bond) $\rightarrow$ intermediates

Sun criterion is also related to melt crystallization. High bond strengths are difficult to break/reform into ordered lattice upon cooling. Hence, oxides having high bond strengths have high viscosity and they are good glass formers.

1.9 Glasses as sealants

Glass and glass–ceramic seals rigidly bond to the cell components, can prevent leakage and mixing of gasses, and are electrically insulating. Additionally, glass and glass–ceramic seals are flexible in design, easy to fabricate, and cost-competitive [46-50]. A wide range of material properties required for sealing can be achieved with a glass or glass–ceramic seal by suitable compositional design. There are four important thermal properties to consider for a SOFC seal glass i.e. T_g , T_s , CTE and devitrification resistance. The T_g value of a seal glass should be slightly below the cell operating temperature to relieve thermal stress and self-heal cracks [10, 51]. A seal glass generally contains 40–70 mol% network formers. T_g and T_s generally increase with SiO_2 content because of a higher amount of bridging oxygen, higher network connectivity, and higher T_g and T_s of vitreous SiO_2 . Presence of planar boroxyl structural groups and low T_g of pure B_2O_3 ($\sim 275^\circ\text{C}$) lead to low T_g for the B_2O_3 –containing glasses [52-53]. B_2O_3 addition increases the fraction of non-bridging oxygen containing borate and silicate structural units. The higher amount of non-bridging oxygen decreases network connectivity and thus T_g and T_s . A seal glass generally contains 20–45 mol% network modifiers. Intermediate oxide is generally between 5–10 mol% for a seal glass. Several additives such as rare earth metal oxides and transition metal oxides are used in seal glass compositions to tailor the thermal properties. Some of these additives are listed in table 1.5. La_2O_3 , a rare earth metal oxide, is commonly used in seal glass compositions.

Table 1.5: Effect of additives on properties of seal glass [54-60].

Oxide	Function
Al ₂ O ₃	Allows control over viscosity through the rate of crystallization
B ₂ O ₃	Reduces T _g , T _s , and viscosity and improves wetting
BaO, SrO	Reduces T _g and T _s , and raises CTE in the glass-ceramic
La ₂ O ₃ , Nd ₂ O ₃ , Y ₂ O ₃	Used as a viscosity modifier and long-term CTE stabilizer
CuO, CoO, NiO, MnO	Improves surface adherence
MgO	Improves surface adherence, Reduces T _g and T _s , and raises CTE in the glass-ceramic
CaO	Reduces T _g and T _s , and raises CTE in the glass-ceramic
Na ₂ O, K ₂ O	Act as effective flux but the alkali cations react vigorously with the fuel cell components like cathodes; have undesirable TEC. Increases conductivity
ZnO, PbO	Improves flux, reducing agent
TiO ₂ , ZrO ₂ , Cr ₂ O ₃ , Ni	Stimulates crystallization
Sb ₂ O ₅	Oxidizing agent
P ₂ O ₅	Decreases volatilization, reduce CTE and mechanical strength

Less than 10 mol% La₂O₃ is sufficient to increase T_g by 30–50 °C although more than 20 mol% has been used in some seal glasses [61-62]. ZrO₂, TiO₂, NiO and ZnO are common transition metal oxides in seal glass compositions. The effect of transition metal oxides on T_g and T_s depends on the specific glass composition [63-64]. T_g and T_s increases when these oxides are network formers and decreases or stay unchanged when these oxides are network modifiers. The CTE of a seal glass should not differ by more than $1 \times 10^{-6} / ^\circ\text{C}$ with the interfacing SOFC components in order to obtain pore and crack-free interface. Devitrification of a seal glass is undesirable as it deteriorates the properties. The origins of devitrification are the very small nuclei formed during glass making, heterogeneity in glass network structure, surface flaws, and residual stress from mechanical polishing. Qualitatively, higher temperature and longer time required for a glass to devitrify mean higher devitrification resistance. Glass network formers can degrade the devitrification resistance of a seal glass in two ways. First, the degree of network connectivity decreases with increased fraction of non-bridging oxygen-containing structural units. Second, coexistence of several different types of structural units induces heterogeneity in a glass network structure [65-66]. Silicate glasses have a higher degree of

devitrification resistance than borate and borosilicate glasses because of their higher glass network connectivity. Localized stresses due to the CTE difference between the devitrified phase(s) and the glass phase are of most concern. These stresses and the lower flowability of the devitrified phases can create pores and cracks in the glass at the interface.

1.10 Interfacial compatibility of glasses

Understanding the composition–structure–property relations of seal glass is the key for suitable seal glass compositional design. Desired thermal properties of SOFC seal glasses have been achieved in several glass systems but long-term stability remains a persistent problem. The performance and durability of SOFCs strongly depend on the seal glass thermomechanical properties such as interfacial strength. Accordingly, thermomechanical properties of the interface should be discussed from interfacial bonding strength point of view. Interfacial reaction kinetics needs to be understood for different glass systems.

Seal glass should wet and bond with electrolyte, electrodes, and metallic interconnects uniformly to form good sealing without any pores or cracks at the interface. The interaction usually involves inter-diffusion and chemical reaction of the elements of the seal glass and the interfacing cell components [67-68]. Severe interaction between the seal glass and the adjacent cell components increases interfacial layer thickness, which in turn leads to formation of pores and crack formation at the interface and delamination of the glass [69-70]. There is no consensus on desired interfacial layer thickness. Interaction of a seal glass with metallic interconnect is more severe than with other cell components [33-36, 58, 61]. Subsequently, seal glass interaction with metallic interconnect has been the focus of most interfacial studies. Chromia forming ferritic stainless steel is the most preferred interconnect [71], which contains 17.0–33.0 wt% Cr with different trade names such as Crofer 22APU, AISI 446, AISI 430, and AL29-4C alloys [56]. Seal glass interaction with interconnect depends on the glass and interconnect compositions, exposed atmospheres, and sealing conditions. For example, a BaO–CaO–borosilicate glass forms a porous interface with cracks with the Crofer 22APU alloy but pore- and crack-free interface with a slightly different alloy composition [72-74]. Pores and cracks at the interface and in the seal glass are gas leakage paths. Localized thermomechanical stress due to the devitrification of the seal glass and severe interaction with the interfacing components increases the numbers of pores and cracks and gas leakage rate. The origin of the porous layer and cracks at the interface is two-fold. First, devitrification causes glass volume

decrease, poor glass flow at the interface, and CTE mismatch between the glass phase and the devitrified phases. Second, the glasses react with the volatile chromium species such as CrO_3 and $\text{CrO}_2(\text{OH})_2$ from the interconnect and form BaCrO_4 and SrCrO_4 [36, 56]. The CTE of these chromate phases ($21.0\text{--}23.0 \times 10^{-6} / ^\circ\text{C}$) are much higher than those of the seal glasses ($10.0\text{--}12.0 \times 10^{-6} / ^\circ\text{C}$). Seal glasses generally wet ZrO_2 electrolyte well. Interfacial stability between a seal glass and ZrO_2 electrolyte is not a problem regardless of glass composition, sealing condition, and atmosphere [75-80]. Seal glass can interact with yttria stabilized zirconia and forms BaZrO_3 / CaZrO_3 / SrZrO_3 [80]. Presence of alkali oxide(s) in a seal glass is undesirable. An alkali silicate glass can react with an interconnect and form alkali chromates (such as Na_2CrO_4 , K_2CrO_4), which vaporize and destabilize glass network [77, 81].

Interfacial interaction study among different components is very important to know the various phase formations at the operating temperature. The nature of resultant phases and their volume may lead to the degradation and reduce the life of SOFC. So interfacial interaction currently needs more attention especially between the sealants and the electrolyte as well as interconnects as it is crucial and important. In addition to this, little attention is paid to the property relations like chemical interaction between the interface of glass sealants with the low temperature electrolyte. However, additional work is required to determine the unwanted effect of this interaction, which leads to interdiffusion, reduced electrochemical activity of cell components and degradation of SOFC performance.

It is necessary to look for the conditions, which inhibit or avoid the formation of detrimental phases. In this work, the major focus is on the chemical compatibility of glass seals with interconnect and electrolytes to understand the mechanisms involved for attaining the long term performance goals. In the present investigation, efforts are made to understand the mechanism of interfacial interaction and their effect on crystallization kinetics, formation of various crystalline phases and their effect on thermal expansion and structural properties.

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CHAPTER 2

LITERATURE SURVEY

Overview

Efforts are being made to search an appropriate sealing material for solid oxide fuel cells. Sealing materials should be electrically insulator and chemically stable up to operating temperature of SOFCs. Among the existing materials, glass and glass ceramics are the best one to be used as sealant under different operating conditions of SOFC. The properties of glass sealants are very sensitive to initial constituents, their mol % as well as chemical nature. However, during operation of SOFC glasses get converted into glass ceramics and some crystalline phases nucleate in the matrix of glass. Sometimes these nucleated phases are detrimental and may exhibit low/high thermal expansion compared to other components of SOFC causing cracks or pores in the glass seal. Therefore, it is important to study the interacting interface for different durations of heat-treatment. In this section, we have summarized the current research in the area of interaction study among the sealants and various components of SOFC like electrolyte and interconnects. Bismuth vanadates being one of the promising low to intermediate temperature range electrolyte, have also been studied to elucidate the most promising electrolyte system for interaction with glasses.

2.1 Crystalline phases in glass sealants

Understanding the fundamental mechanisms involved in creation and destruction of glassy state is impossible without understanding the nucleation and crystallization kinetics [1-5]. Glass gets converted to glass ceramics during operation of SOFC at high temperature. Glass ceramics possess superior mechanical properties compared to glass and have very different CTE, due to nucleation of different crystalline phases in different volume fraction. The crystallization behavior of the glass-ceramics can be classified into two categories. One consists of relatively slow and consequently, stable crystallization with the long-term operation. The other is relatively rapid crystallization that occurs progressively up to 1000 h. The latter behavior is thought to be unsuitable for long-term operation of SOFC.

Rapid and progressive crystallization of a glass during cell operation can deteriorate the fluidity of the glass because of significant decrease of the residual glass matrix. It can lead thermal expansion mismatch, especially if the CTE value of the increasing crystalline phase differs significantly from that of the parent glass. To develop a good sealant, it is therefore, necessary to understand the crystallization kinetics both from the point of view of their sealing properties and their chemical interactions when in contact with other components of the cell [6-7]. Table 2.1 lists some of the crystalline phases that precipitate in various glass systems.

Table 2.1: Various crystalline phases and their CTE.

System	Crystalline phase	CTE ($\times 10^{-6}/^{\circ}\text{C}$)
Ba-Si-O [8]	Barium silicate (BaSiO_3)	9-13
	Barium orthosilicate (BaSi_2O_5)	14
Mg-Si-O [9-10]	Enstatite (MgSiO_3)	7-9
Ca-Si-O [9-11]	Wollastonite (CaSiO_3)	4-9
	Calcium orthosilicate (Ca_2SiO_4)	10-14
Ba-Ca-Si-O [8]	Barium calcium orthosilicate ($\text{Ba}_3\text{CaSi}_2\text{O}_8$)	12-14
Mg-Al-Si-O [9-10]	Cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$)	2
	Cristobalite (SiO_2)	2.32
Sr-Al-Si-O [12-13]	Hexacelsian ($\text{SrAl}_2\text{Si}_2\text{O}_8$)	8-11
	Monocelsian ($\text{SrAl}_2\text{Si}_2\text{O}_8$)	3
	Orthocelsian ($\text{SrAl}_2\text{Si}_2\text{O}_8$)	5-8
Ba-Al-Si-O [8,10,12]	Hexacelsian ($\text{BaAl}_2\text{Si}_2\text{O}_8$)	7-8
	Monocelsian ($\text{BaAl}_2\text{Si}_2\text{O}_8$)	2-3
	Orthocelsian ($\text{BaAl}_2\text{Si}_2\text{O}_8$)	5-7
Ba-Mg-B-Si-O (with Zn) [14]	Barium silicate ($\text{Ba}_2\text{Si}_2\text{O}_4$)	-
	Barium magnesium silicate (BaMgSiO_4)	-
	Barium magnesium silicate ($\text{Ba}_2\text{MgSiO}_3$)	-
	Barium zinc silicate ($\text{BaZn}_2\text{Si}_2\text{O}_7$)	-

Ba-Ca-Al-B-Si-O [15]	BaCrO ₄ with chromia forming alloys	$\alpha_a = 16.5$ $\alpha_b = 33.8$ $\alpha_c = 20.4$
Ba-Mg-Al-B-Si-O [16]	Barium zirconate (BaZrO ₃) Calcium zirconate (CaZrO ₃) Kurchatovate (CaMgB ₂ O ₅)	7.9 10.3 10.4
Na-Ca-Al-B-Si-O [17]	Gehlenite (Ca ₂ Al ₂ SiO ₇) Nepheline (AlNaSiO ₄) Corundum (Al ₂ O ₃)	- - -

2.2 Glass systems and their interaction with interconnect/electrolytes

Glasses and particularly glass–ceramics are ideal sealant candidates as their properties including thermal expansion can be tailored to make it compatible with the other components of fuel cell. Glass–ceramics offer the additional advantage of higher operating temperatures. Some potential compositions of glasses employed as sealants in SOFC are summarized in table 2.2, and their selected properties are listed in table 2.3.

Table 2.2: Potential glass compositions (in wt%) for SOFC.

Glasss-code	Na ₂ O	MgO	CaO	BaO	SrO	Cr ₂ O ₃	ZnO	B ₂ O ₃	Al ₂ O ₃	SiO ₂	Y ₂ O ₃	La ₂ O ₃
Alkaline earth borate												
14a [18]	-	20	20	10	-	-	-	40	10	-	-	-
MA1 [19]	-	8.1	-	-	-	-	-	33.9	9.4	-	-	48.6
BM1 [19]	-	10.5	-	45.6	-	-	-	43	-	-	-	-
BMA1 [19]	-	6.0	-	6.7	-	-	-	32.2	8.9	-	-	46.2
BM2 [19]	-	9.7	-	50.1	-	-	-	40.2	-	-	-	-
Alkaline earth silicate												
BCAS4 [20]	-	-	9.2	55.6	-	-	-	-	5.5	25.3	-	-
BCAS5 [20]	-	-	8.8	57.4	-	-	-	-	5.4	22.1	-	-
7A [21]	-	16.9	18.82	6.43	-	-	-	-	2.14	47.88	-	6.83
7(Sr)-2B [22]	-	16.9	18.83	-	4.35	-	-	2.0	2.14	47.92	-	6.84

7A-Cr [21]	-	16.82	18.72	6.40	-	0.5	-	-	2.13	47.64	-	6.80
10B [23]	-	16.48	18.34	6.27	-	0.5	-	2	2.08	46.67	-	6.66
10C [23]	-	16.14	16.85	9.21	-	0.5	-	2	2.04	45.73	-	6.53
G18 [15,24-26]	-	-	8.8	56.4	-	-	-	7.3	5.4	22.1	-	-
YSO-4 [27]	-	-	3.7	-	42.2	-	2.7	9.3	-	27.2	14.9	-
Glass 27 [28]	-	-	15	-	26.6	-	15	1.9	4.1	35.2	-	-
Mg1.5-55 [14]	-	8.9	-	60.7	-	-	-	-	-	40.4	-	-
Mg1.5- 40.5B- 10Pb [14]	-	7.4	-	42	-	-	-	3.5	-	24.4	-	-
Mg1.5- 40.1B-8Zn [14]	-	4.7	-	47.9	-	-	7.5	12.1	-	27.8	-	-
Alkali Alkaline earth silicate												
SACN [17,29]	9-12	-	20-25	-	-	-	-	-	10-14	50-55	-	-
SACNZn [30]	1.2	0.27	31.6	-	-	-	9.1	-	19.4	38.4	-	-
Alkaline earth boro- silicate												
L2 [6]	-	-	-	47.4	-	-	-	10.3	9	17.7	-	15.6
LO6 [31]	-	-	-	20	-	-	-	60	5	15	-	-
LO9 [31]	-	-	-	50	-	-	-	30	5	15	-	-
SrLaB [32]	-	-	-	-	15.2	-	-	20.5	9	3.5	-	51.8
MA12 [19]	-	8.4	-	-	-	-	-	8.8	9.7	22.7	-	50.4
VS1 [33]	-	-	-	-	33.9	-	-	15.2	-	26.2	24.7	-
VS2 [33]	-	-	-	-	29.8	-	-	13.4	-	23	-	33.8

VM1 [33]	-	16.6	-	-	-	-	-	19.2	-	33.1	31.1	-
VM3 [33]	-	20.1	-	-	-	-	-	23.1	16.9	39.9	-	-
BaBSi [34]	-	-	-	50	-	-	-	19.9	-	24	1.9	2.2
23 [24]	-	-	6.6	46.7	-	-	-	8.1	2.4	19.7	-	16.5
L09 [31]	-	-	-	68.6	-	-	-	18.7	4.6	8.1	-	-
P00 [31]	-	-	-	25.3	-	-	-	15.1	10.1	49.5	-	-
A2 [35]	-	-	-	60.6	-	-	-	12.6	5	21.8	-	-
17 [18]	-	3.9	5.5	23.9	-	-	-	17.4	7.7	15.1	-	26.5
Glass 59 [28]	-	-	-	34.3	23.2	-	-	15.6	-	26.9	-	-
AO [35]	-	-	-	61.8	-	-	-	14	-	24.2	-	-
A2 [35]	-	-	-	60.6	-	-	-	12.6	5	21.8	-	-

Table 2.3: Properties of glass sealants for SOFC.

Glass code	T _g (°C)	T _c (°C)	T _s (°C)	Density (g/cm ³)	CTE (x 10 ⁻⁶ /°C)
18 [24]	-	630	685		10.8
SACNZn [30]	700	780	900	-	9.7
Mg 1.5-55 [14]	715	-	750	3.15	10.1
Mg1.5-40.5B-10Pb [14]	-	-	512	5.44	-
Mg1.5-40.1B-8Zn [14]	616	-	633	1.97	-
Glass A [36]	470	-	560	2.5	10.4
Glass C [36]	600	-	720	-	10.7
AO [35]	622	763	907	-	10.83
A2 [35]	602	830	-	-	10.67
MBS [37]	-	-	700	-	10
L2 [6]	655	862	710	-	11.1
10B [23]	755	904	-	3.06	8.4
10C [23]	756	906	-	3.1	8.71
17 [18]	620	-	-	-	8.8
14a [18]	576	-	-	-	9.4
GC-9 [38]	668	820	864	745	-
BCAS4 [20]	609	755	672	3.89	11.9

BCAS5 [20]	608	720	660	3.93	12.4
7A [21]	685	912	716	3.08	8.69
MA1 [19]	621	887	671	-	9.01
MA12 [19]	638	907	723	-	8.33
BMA1 [19]	620	785	656	-	9.66
BM1 [19]	530	804	616	-	10.06
BM2 [19]	582	845	593	-	11.1
7A-Cr [21]	675	895	721	3.08	8.48
VS1 [33]	626	-	-	-	7.36
VS2 [33]	620	-	-	-	5.26
VM3 [33]	735	-	-	-	1.99
LO9 [31]	-	-	3.92	-	10.96

Ley et al. [38] studied $\text{SrO-La}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$ glass system. The CTE for these materials were in the range of $(8\text{--}13) \times 10^{-6} / ^\circ\text{C}$, and these sealant materials bonded well with the ceramics of the SOFC and more importantly, formed bonds that could be thermally cycled without failure. Larsen and James [39] determined the thermal properties, glass forming tendency and glass stability for four different refractory $\text{MgO/CaO/Cr}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ phosphate based glasses in relevant atmosphere of SOFC. Also, the bonding ability and interaction as a function of temperature between the glasses and $\text{La}_{0.8}\text{Ca}_{0.22}\text{CrO}_3$ interconnect material have been studied which revealed that the bonding ability and interface interaction is closely related to CaO content. The crystallization kinetics of $\text{AO-Al}_2\text{O}_3\text{-SiO}_2\text{-B}_2\text{O}_3$ glasses ($\text{A} = \text{Ba, Ca, Mg}$) was investigated [7,40-42]. In addition to this, the influence of nucleating agents such as TiO_2 , ZrO_2 , Cr_2O_3 , and Ni on MgO base glasses was elucidated [7]. The activation energy of crystal growth, E_a , varied between 330 and 622 kJ/mol. The nucleating agents tend to enhance E_a except ZrO_2 . An increase of the Al_2O_3 concentration induced phase separation and decreased E_a . The most encouraging result was the complete absence of cordierite phase ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) in all powder mixtures composed of the sealant with Cr_2O_3 as the nucleating agent. They also reported the chemical interactions of the candidate sealants with 8-mol% yttria stabilized zirconia (8YSZ), Ni and the oxide dispersion strengthened (ODS) alloy [43]. It was observed that MgO base sealants exhibit superior properties as compared to BaO and CaO base sealants because of higher activation energy of crystal growth.

Demirkesen and Maytalman [44-45] also studied the effect of partial replacement of ZnO by Al_2O_3 on the crystallization behaviour and bending strength of Li_2O - ZnO - SiO_2 glass-ceramic. The maximum bending strength of 290 MPa was obtained for composition containing 4 wt% Al_2O_3 , above which a marked decrease was determined. Acid resistance upto greater extent was obtained by using 6 wt% Al_2O_3 for the glass and 11 wt% for the glass-ceramic. Sohn et al. [6] investigated the thermal and chemical stability of BaO – Al_2O_3 – La_2O_3 – B_2O_3 – SiO_2 glass system as well as bonding characteristics and wetting behavior to YSZ electrolyte. In continuation to this work, 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 and NiO [46]. No interface reaction was observed for all the glass/YSZ specimens heat-treated at 800–850 °C up to 100 h.

The interaction of 35BaO - 15CaO - 5 Al_2O_3 -10 B_2O_3 – 35 SiO_2 (BCAS) glass system with both the chromia- and alumina-forming alloys was investigated by Yang et al. [15]. For all chromia-forming alloys, chromium or chromia dissolved into the BCAS sealing glass and formed a chromium rich solid solution. For alumina-forming alloys, no formation of barium chromate was observed but pores in the seal could be seen whereas with YSZ electrolyte, the glass-ceramic exhibited good chemical compatibility. The glass formation areas of the systems RO – BaO – SiO_2 ($\text{R} = \text{Mg}, \text{Zn}$) have been investigated by Lara et al. [47-48]. The non-isothermal sintering and crystallization kinetics were also studied for four glasses in the system 50 SiO_2 – (45-x) BaO –x RO –5 Al_2O_3 ($\text{R} = \text{Ca}, \text{Mg}, \text{Zn}$ and $x = 0, 15$) (mol%) by this group [48-49]. The studied glasses presented good dilatometric and viscosity properties for this application though Ca and Mg based glasses exhibited undesirable expansion during the crystallization process.

Pascual [14] also studied the glass–ceramic (Mg1.5–55) of composition 55 SiO_2 –27 BaO –18 MgO (mol%) and its bonding and chemical compatibility with Crofer 22APU. The above glass composition was further modified with addition of ZnO. All the glasses present a suitable CTE for use in SOFCs. Compositions Mg1.5–40–15B and Mg1.5–40–15B–8Zn exhibit the best glass–ceramic/Crofer 22 APU union for the operating temperature of 850 °C. Crystallization kinetics of barium–calcium aluminosilicate glass (BCAS) have been investigated by differential thermal analysis (DTA) by Bansal and Gamble [50]. BaSiO_3 and hexacelsian ($\text{BaAl}_2\text{Si}_2\text{O}_8$) were the primary crystalline phases whereas monoclinic celsian ($\text{BaAl}_2\text{Si}_2\text{O}_8$) and $(\text{Ba}_x\text{Ca}_y)\text{SiO}_4$ were also detected as minor phases. Needle-shaped BaSiO_3 crystals are formed first, followed by the formation of other phases during longer time of heat treatments. The feasibility of adding micron-scale YSZ powders to modify the properties of two borate glasses i.e. 40 B_2O_3 –10 Al_2O_3 –

20MgO-20CaO-10(BaO–SrO) for the Ba and Sr-compositions was investigated by Brochu [16] to seal electrolyte supported SOFCs. Ba-containing glass reacted with YSZ to form a BaZrO₃ compound. On the other hand, the reaction involving the Sr-containing glass with the YSZ additive shows the formation of calcium zirconate (Ca is an ingredient in both glasses) initially followed by appearance of strontium zirconate with further heating.

According to Fergus [51], the flow characteristics, thermal expansion behavior and crystallization kinetics of sealing materials can be controlled by proper glass composition. Alternative sealing approaches has been suggested by him for overcoming the inherent brittleness of glass–ceramic materials. Brief review of the requirements for SOFC seals and a new concept of self-healing seals has been proposed for creating seals for planar SOFC [26, 36, 52]. Experiments done by Haanappel [53] revealed that the chemical and electrical behavior of the sandwich samples strongly depends on the experimental conditions. Several low thermal expansion Fe–Co–Ni alloys including HRA 929C, Thermo-Span and EXP 4005 were evaluated as interconnect for IT-SOFC [54]. New joining approach like the bonded compliant seal (BCS) and reactive air brazing for hermetically sealing the cell and window frame components in pSOFC stacks has been proposed [8, 55-56].

Meinhardt et al. [24] investigated a series of barium aluminosilicate glasses modified with CaO and B₂O₃. These glasses were evaluated for their suitability with respect to thin gauge stainless steel (FeCrAlY and 446, both ferritic alloys). A reaction zone has developed between the sealant and the steel comprising of both chromia and alumina. Milhans [25, 57] has done a full statistical analysis of the microstructure of glass–ceramic SOFC seal material G18, which is a barium–calcium–aluminosilicate (BCAS)-based glass with added boron oxide for better control over the CTE and viscosity.

Goel et al. [58] investigated the suitability of three new glass compositions for producing diopside–Ca-Tschermak clinopyroxene based glass–ceramics (GCs). The effect of La₂O₃ and Cr₂O₃ on the processing and characterization of four glasses and the derivative GCs in the diopside system was also studied [21]. The CTE of all four glasses was observed to be higher than their La₂O₃ and Cr₂O₃ free analogs. The E_a values for Cr₂O₃ containing glasses were found to be lower than their Cr free analogs. Good compatibility of these glasses with Crofer 22 APU and YSZ has been obtained. Goel et al. [59-61] appraised diopside (CaMgSi₂O₆) based glass-ceramics in the system SrO–CaO–MgO–Al₂O₃–B₂O₃–La₂O₃–Bi₂O₃–SiO₂ for sealing applications in SOFC. Well-sintered GCs comprised of orthocelsian (OC) and hexacelsian (HC) after

sintering at 850 – 900 °C for 1 h was obtained. These GCs exhibited negligible interfacial reaction with YSZ and the good matching of CTEs was observed for glass ceramics. After modifying the parent composition ($\text{Ca}_{0.9}\text{MgAl}_{0.1}\text{La}_{0.1}\text{Si}_{1.9}\text{O}_6$) with Cr_2O_3 and BaO [22-23], extensive segregation of oxides of Ti / Mn at the interface of the Crofer22 APU interconnect alloy, along with negligible formation of BaCrO_4 between GC/interconnects diffusion couples is observed. In addition to this, thermal stability and crystallization kinetics of glass 21 mol% MgO, 21.36 mol% Al_2O_3 , 53.32 mol% SiO_2 and 4.11 mol% TiO_2 was studied and it was found that TiO_2 favorably influences the nucleation of μ and α -cordierite crystalline phases in the glass system [62].

Batfalsky et al. [63] studied a short-term degradation effect caused by unwanted chemical interaction between glass–ceramic sealants and ferritic steel interconnects. The stack tests suggested that an increase in the Si content increases the corrosion rate and thus deteriorate the stack performance. Nielsen et al. [64] optimized composite seals with long-term compliancy based on the sodium aluminosilicate (NAS) glass with MgO-filler. It showed promising results in terms of both the bonding strength and interface reactivity between metal and glass. Both pure NAS glass applied as thin film sealings and NAS/MgO composite material applied as CTE-matched seal components developed gas tight sealing performance, when sealed at 950 °C. The NAS/MgO composite material showed self-healing properties after thermal cycling.

Wang et al. [65] studied a glass system based on SiO_2 – B_2O_3 – Al_2O_3 – BaCO_3 – PbO_2 – ZnO and optimized the composition exhibiting best performance named as AF8 whose technical thermal expansion coefficient (t-CTE) between 50 and 500 °C is $10.58 \times 10^{-6} / ^\circ\text{C}$. It could adhere well with YSZ having no pores in the sealant. Gross [66] focused the investigations on a composite material consisting of zirconia in a glass matrix based on the system BaO–CaO– SiO_2 (BCS). Stack test performed with this new material, at 800 °C over a period of 1000 h during five thermal cycles proved good sealing properties. Malzbender [67] did symmetric shear and indentation test to characterize the critical shear stress of the glass-ceramic BaO–CaO– Al_2O_3 – SiO_2 at SOFC operating temperature. The investigations showed that the sealant exhibits viscous shear deformation at 800 °C, a temperature typical for SOFC operation [68]. Addition of Y_2O_3 increased the glass transition temperature T_g , crystallization temperature T_c and stability of the glasses. It further suppressed the formation of cordierite in SiO_2 –MgO– B_2O_3 – Y_2O_3 – Al_2O_3 system [69]. BaO–CaO– Al_2O_3 – SiO_2 – La_2O_3 – B_2O_3 glass-ceramic sealant materials developed by Jinhua et al. [70] showed superior stability and compatibility with the Lanthanum strontium

gallate manganite (LSGM) electrolyte during operation of SOFC. Alkali glass systems and barium free silica based glasses were extensively investigated by Smeacetto et al. [17, 29-30]. They studied two sodium–calcium–aluminosilicate glasses (SACN1 and SACN2) to develop glassy seals. SACN1 glass results in a low quality seal with detached interface between the glass matrix and the pre-oxidized AISI 430 steel. The interfacial adhesion of SACN2, which has CTE close to AISI 430, with pre-oxidized AISI 430 was better. Chou and Stevenson [71-72] studied novel Sr-Ca-Ni-Y-B silicate sealing glass for SOFC. The interfacial microstructure showed no distinct reactions at the interfaces of glass/YSZ or glass/metal, though some segregation of Ni was found along the glass/metal interface.

Cheng et al. [73] studied lead borate low temperature sealing glasses. Glass with good mechanical properties at a sealing temperature of 430 °C can be obtained by the addition of 2 mol% ZnO and 2 mol% Bi₂O₃. Several compositions based on BaO–CaO–Al₂O₃–SiO₂ (BCAS) and BaO–Al₂O₃–SiO₂ (BAS) glass system have been studied by Ghosh et al. [19-20, 74]. These glasses are found to be well adhered with metallic interconnects, such as commercial ferritic steel (Crofer 22APU), at an optimum sealing temperature of 850 °C. One of the developed compositions having MgO and BaO content of 22 and 25 mol% respectively, with a glass former ratio of 3 (SiO₂:B₂O₃) has been found to be quite promising in terms of its mechanical property, excellent joining and minimum chemical interaction with the metallic interconnect such as Crofer 22APU.

Arora et al. [75] studied the thermal behavior and crystallization kinetics of the glass BZAS with composition 30BaO–20ZnO–2.5Al₂O₃–7.5B₂O₃–40SiO₂ (mol%). Barium zinc silicate (Ba₂Zn₃Si₃O₁₁) and barium aluminum silicate (BaAl₂Si₂O₈) were found to be the predominant phases after the heat treatment of the glass powder for 30 mins at 800 °C. They also studied glass series of compositions in the system 40SiO₂–30BaO–20ZnO–(x)Mn₂O₃–(10-x)B₂O₃ glasses [76]. Concentration of Mn₂O₃ > 7.5 mol% induced phase separation in the glass matrix. Thermodynamically stable hexacelsian and monoclinic phases are formed which are not detrimental to SOFC application.

Mahapatra et al. [77-78] investigated thermochemical compatibility of SrO–La₂O₃–Al₂O₃–SiO₂ based glass (SABS-0) with Crofer 22APU, nickel, and NiTiHf alloy for SOFC applications. Extensive devitrification of SABS-0 is observed at the NiTiHf/SABS-0 interface. Chromium in the Crofer 22APU alloy participated in the chemical reaction with the SABS-0 glass where La₂Cr₂O₉ formed at the interface and Sr₇Al₁₂O₂₅ crystal phase formation occurred in the glass

matrix. The interfacial compatibility of an alkaline earth silicate glass (SABS-0) with $(\text{Mn,Co})_3\text{O}_4$ coated Crofer 22APU and AISI 441 interconnects at 800 °C for 100 h in argon, air, and $\text{H}_2/\text{H}_2\text{O}$ atmospheres was also demonstrated [79-80]. Detailed microstructural and diffusion studies showed that the interfacial compatibility is better for the $(\text{Mn,Co})_3\text{O}_4$ coated Crofer 22APU alloy but deteriorates from the $\text{H}_2/\text{H}_2\text{O}$ to the air or the argon atmospheres for both alloys. Hoyt [81] also studied $\text{Co}_{1.5}\text{Mn}_{1.5}\text{O}_4$ spinel ceramic coatings to extend the lifetime of stainless steel. Preoxidation was found to inhibit Fe and Cr transport from the stainless steel into the coating and preoxidized samples exhibited a substantially thinner surface layer after oxidation.

Namwong [82] studied a barium-calcium silicate glass for use as seals in pSOFCs where $\text{BaAl}_2\text{Si}_2\text{O}_8$ (hexacelsian), BaSiO_3 and $\text{BaCa}_2\text{Si}_3\text{O}_9$ phases precipitated out. Adhesion test between the glass and the other components including YSZ and stainless steel grade AISI 430 revealed that good union was achieved. Wang et al. [31] studied the feasibility of using MgO , KAlSi_2O_6 , and KAlSiO_4 to tune the CTE of $\text{BaO-Al}_2\text{O}_3\text{-SiO}_2\text{-B}_2\text{O}_3$ glasses. Alkaline earth metals free $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$ glass has been investigated to relieve the poison caused by BaCrO_4 or SrCrO_4 formation [83]. The CTE value dropped with the rise in SiO_2 content and escalated with increase in La_2O_3 content. The composites of selected $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2\text{-B}_2\text{O}_3$ glasses and SDC additive on the YSZ substrate showed quite promising results. Zhang [84] investigated the interaction using model reactions between Cr_2O_3 and glass powders in order to reduce the chromate formation. It is found that the addition of MnO_2 reduces the formation of SrCrO_4 more significantly than that of ZnO and La_2O_3 , within the SOFCs operational temperature range. Indentation creep tests of Ba-B-Si-Al-O glass used for intermediate-temperature SOFC revealed newtonian flow behavior at 600–630 °C [85]. The force–displacement curves of non-aged sintered GC-9 glass estimated the T_g between 700 °C and 750 °C, while that of the aged one is between 750 °C and 800 °C [86]. Due to a crack healing effect of the residual glass at higher temperature, sintered GC-9 glass exhibits flexural strength greater than that at room temperature in between 650 °C to T_g . Glass based on $\text{Y}_2\text{O}_3\text{-BaO-Al}_2\text{O}_3\text{-SiO}_2\text{-B}_2\text{O}_3$ (YBA) is found to adhere well with other cell components, such as electrolytes and stainless steels, at an optimum sealing temperature of 800 °C [87].

Ojha et al. [88] appraised a series of SOFC glass sealants with composition SrO (x), La_2O_3 (15), Al_2O_3 (15), B_2O_3 (40–x), and SiO_2 (30) [$x = 10, 15, 20, 25$ and 30] (wt%) [SLABS]. Increased

substitution of B_2O_3 by SrO in the glasses caused increase in the density, T_g and T_s . On the other hand, the crystallization temperatures showed a decreasing trend and CTE increased with increasing substitution. Kerstan [89] studied some high thermal expansion seal systems using high-temperature X-ray diffraction. These systems are binary calcium silicates, $CaSiO_3$, $Ca_3Si_2O_7$ and Ca_2SiO_4 zinc silicates, Zn_2SiO_4 , ternary silicates of BaO , CaO and ZnO ; $BaCa_2Si_3O_9$, $Ca_2ZnSi_2O_7$, and one quaternary silicate, $Ba_2CaZn_2Si_6O_{17}$. Only $CaSiO_3$, $Ca_3Si_2O_7$ and $BaCa_2Si_3O_9$ exhibit CTE in the range suitable for high thermal expansion seals.

In order to improve the sinterability and electrical conductivity of $La_{0.8}Ca_{0.2}CrO_3$ (LCC), LCC/glass composite interconnect materials for high temperature solid oxide fuel cells (SOFCs) were studied by Pi [90]. The Crofer 22APU treated at 1100 °C in N_2 with 10 vol% H_2 showed long-term stability and a lower ASR value than other samples (heat-treated at 800 °C and 900 °C). Ye et al. [91] studied the effect of Al_2O_3 on glass-based composite seal. The interfaces of interconnect/seals, electrolyte/seals and anode/seals remained well adhered and integrated with each other, which is highly beneficial to block gas leakage. Dai et al. [92] fabricated Al_2O_3 -based compressive seals by tape casting with Al_2O_3 and 0-30 wt% aluminum powders. The interfaces in the interconnect/seal/ cell assembly with the ACS3 seal retained integrity even after 50 thermal cycles, demonstrating the applicability of the Al_2O_3 -based compressive seals in the planar intermediate temperature SOFCs.

2. 3 Intermediate temperature bismuth vanadate electrolytes

Many researchers [93-96] have synthesized various low-intermediate temperature, metal ion doped bismuth vanadate (BIMEVOXes) solid electrolytes and monitored their suitability and applicability in SOFC. In the following section, sequential development of solid electrolytes for its application in electrochemical devices has been reviewed.

Abraham et al. [97] studied the conduction mechanism and solid solution formation in terms of the defect structure of the BIMEVOXes. Based upon two theoretical models, they proposed a general defect equation to form the solid solution. Basically, these models consist of Equatorial Vacancy (EV) model and Apical Vaccumcy (AV) model in which vacancies are assumed to be located exclusively in the bridging sites and non-bridging apical sites in the vanadate layer, respectively. The solid solution limits are found to vary not only with charge of the dopant ion, but also with the coordination number of the metal dopant. In most cases it is found that the EV model yields theoretical solid solution limits close to experimental values. Abrahams et al. [98]

also proposed the conduction mechanism in divalent substituted BIMEVOXes system. The main theme of this model is polarizability and arrangement of the Bi $6s^2$ lone pairs, variable coordination of V in oxide systems and the large vacancy concentration in the vanadate layer. This unique combination in the BIMEVOXes enables high ionic conductivity at lower temperature than other electrolytes. This involves positional exchange of oxygen ions with vacancies in the equatorial plane of the vanadate layer. Abraham et al. [97-98] are the first who investigated the structure of $\text{Bi}_4\text{V}_2\text{O}_{11}$. According to them, $\text{Bi}_4\text{V}_2\text{O}_{11}$ consists of Bi_2O_3 layers interleaved with the perovskite like sheets of V_2O_5 with the perovskite slab containing oxygen vacancies V_o responsible for the high oxide ion conductivity. The vanadium is in a highly distorted octahedral site. This system exhibit very complicated structure.

Hu et al. [99] investigated Bi_2O_3 based compositions for the intermediate temperature range. Various authors reported four polymorphs of Bi_2O_3 viz: α , β , γ and δ in the literature [100-101]. Doped Bi_2O_3 based systems have higher conductivity than YSZ at the same temperature [102-105]. In these systems, the high conductivity δ (FCC) phase can be stabilized by using various dopants such that aliovalent. Doped Bi_2O_3 has highest conductivity as compared to any other known solid electrolyte system. Takahashi et al. [106] examined the electrical conductivity, ionic transference number and phase equilibrium of $\text{Bi}_2\text{O}_3\text{-M}_2\text{O}_5$ ($\text{M} = \text{V}, \text{Nb}$ and Ta). The initial work of Debreuille-Gresse [107] for the phase equilibrium of $\text{Bi}_2\text{O}_3\text{-V}_2\text{O}_5$ showed a BiVO_4 phase. Lu and Steele [108] investigated ionic conductivity behaviour of BiVO_4 systems. Doped BiVO_4 systems showed good ionic conductivity at lower temperatures.

The work on BiVO_4 and $\text{Bi}_4\text{V}_2\text{O}_{11}$ systems has been extensively investigated by many researchers due to its attracting transport properties. The dopants in the family of Me^{2+} have been the most widely investigated. All other dopants have been listed in figure 2.1. Copper doped $\text{Bi}_4\text{V}_2\text{O}_{11}$ is the most attractive and first member of BIMEVOX family because of its very high conductivity ($10^{-2} \text{ S cm}^{-1}$ at 350°C) [120]. Abraham et al. [98] studied the $\text{Bi}_2\text{V}_{1-x}\text{Cu}_x\text{O}_{5.5-3x/2}$ series from $x = 0 - 0.12$. However, from $x = 0.07$ to 0.12 , the compound was observed to be highly conducting γ - $\text{Bi}_4\text{V}_2\text{O}_{11}$ phase at room temperature. The conductivity of $\text{Bi}_2\text{V}_{0.9}\text{Cu}_{0.1}\text{O}_{5.35}$ was found to be $3 \times 10^{-3} \text{ S cm}^{-1}$ at 237°C . Variation of conductivity in a limited range of temperature has been reported by Simmer et al. [121], when aged at room temperature. According to them [121] copper-substituted bismuth vanadate ($\text{Bi}_2\text{V}_{0.9}\text{Cu}_{0.1}\text{O}_{5.35}$), known as BICUVOX, possesses high oxygen ion conductivity at 300°C . In the literature, some ambiguity was reported on the dopant concentration, which is necessary to stabilize the

tetragonal γ - phase. According to Pernot et al. [117], tetragonal phase can be stabilized at 7% of Cu doping whereas Goodenough et al. [109] and Lee et al. [122] reported a higher value (15%) of the dopant to stabilize the same phase. Doping on the desired sites in $\text{Bi}_4\text{V}_2\text{O}_{11}$ system [122-123] is very important. In most of the cases, it is assumed that vanadium is replaced without disturbing the bismuth oxide layer.

H																He	
Li [110]	Be											B [112]	C	N	O	F	Ne
Na [93-94]	Mg [109, 97-98]											Al [109, 112]	Si	P [95]	S	Cl	Ar
K [126]	Ca [122]	Sc	Ti [109-111, 129, 131]	V	Cr [114, 112]	Mn [111, 131]	Fe [127]	Co [112-114]	Ni [116-117]	Cu [115-119]	Zn [110-115]	Ga [124]	Ge [110]	As	Se	Br	Kr
Rb	Sr [124]	Y [112, 122]	Zr [109-111]	Nb [109]	Mo 114, 134]	Tc	Ru	Rh	Pd [130]	Ag [123, 128]	Cd	In [112]	Sn [111]	Sb [114]	Te	I	Xe
Cs	Ba	La [112, 124]	Hf [128]	Ta [109]	W 114, 123, 128]	Re	Os	Ir	Pt	Au	Hg	Tl	Pb [111]	Bi [126]	Po	At	Rn

Figure 2.1: Various dopants used in BIMEVOX.

Based on $\text{Bi}_2\text{O}_3\text{-V}_2\text{O}_5\text{-MeO}$ ($\text{Me} = \text{Co}, \text{Cu}, \text{Zn}, \text{Ca}, \text{Sr}$) phase diagrams, Lee et al. [124,122] examined the probability of dopant occupancy in $\text{Bi}_4\text{V}_2\text{O}_{11}$ system. They concluded that the $\text{Bi} \leftrightarrow \text{V}$ and $\text{Me} \leftrightarrow \text{Bi}$ may also take place in addition to $\text{Me} \leftrightarrow \text{V}$ substitution depending upon the substituting cation. The similar conclusion was also drawn by Lazure et al. [114] for $\text{Bi}_2(\text{V}_{1-x-y}\text{Co}_x\text{Bi}_y\text{O}_z)$. According to them, maximum cobalt doping ($x = 0.25$) was associated with a slight bismuth excess ($y = 0.04$) in this system. Reseilhauber et al. [125] observed the effect of grain size and processing condition on the ionic properties of BICUVOX and reported the difference in the conductivity between the large grains and small grains in the fired ceramic material. Anne et al. [116] and Pernot et al. [117] also studied the structure and conductivity of $\text{Bi}_4\text{V}_2\text{O}_{11}$ with Cu and Ni dopants and reported that the high temperature γ - phase with highest conductivity could be stabilized at room temperature. The effect of Zn and Ni substitution on conductivity in

Bi₄V₂O₁₁ system was studied by Kurek et al. [132]. The conductivity values have been reported to be $1.28 \times 10^{-4} \text{ S cm}^{-1}$, $1.19 \times 10^{-4} \text{ S cm}^{-1}$ for Zn and $3.05 \times 10^{-4} \text{ S cm}^{-1}$, $2.78 \times 10^{-4} \text{ S cm}^{-1}$ for Ni substitution during heating and cooling cycles at 227 °C, respectively. Decreasing trend in conductivity with time was also observed for BIZNVOX during heating and cooling in certain temperature ranges. The conductivity reported for La and Al-substituted Bi₄V₂O_{11-δ} on vanadium site is $1.4 \times 10^{-4} \text{ S cm}^{-1}$ at 300 °C and $1.1 \times 10^{-1} \text{ S cm}^{-1}$ at 600 °C, respectively [126]. The doping of Cr³⁺ for V⁵⁺ in Bi₄V₂O₁₁ compound could not stabilize the γ-phase at room temperature. When the substitution of x in Bi₄V_{2-x}Cr_xO_{11-δ} is > 0.05, β-phase was suppressed and α ↔ γ phase transition occurred [127]. Moreover, the conductivity also decreases drastically for this particular dopant. Substitution for V⁵⁺ with Fe³⁺ leads to α, β and γ- phase stabilization [127]. The stabilization of β and γ-phases depend on the amount of iron. The best value of ionic conductivity of the order of $10^{-4} \text{ S cm}^{-1}$ at 300 °C was observed in the composition range of $0.1 \leq x \leq 0.5$ [127].

γ - phase can also be stabilized with MnO₂ in bismuth vanadate when doping occurs on the vanadium site [133-134]. Goodenough et al. [109] and Joubert et al. [135] made isovalent M⁵⁺ substitution such as Sb, Nb and Ta leading to the bigger domain of solid solution. This bigger domain observed is due to the equality of charge between the dopant cation and V⁵⁺ cation. Antimony exhibits higher value of the ionic conductivity i.e. 10^{-2} Scm^{-1} at 320 °C than niobium. The ionic conductivity values are comparable to those obtained with the best BIMEVOX (ME = Cu or Ti). Uranium is the first substituent (V⁵⁺ ↔ U⁶⁺) that allows the stabilization of γ-type compounds [136-137]. Substitution of U⁶⁺ for V⁵⁺ involves a decrease of oxide ion vacancies, but as demonstrated by Lazure et al. [114], the BIMEVOX properties are more sensitive to the dopant ability to affect the long range ordering of the parent compound Bi₂VO_{5.5} than to radius and valency state of the dopant. However, Vannier et al. [128] showed that γ – phase could be formed up to substitution of 0.225 with high ion conductivity in the Bi₄V_{2-x}Mo_xO_{11-δ}. They obtained solid solution of α-phase for x < 0.05 while β-phase in the range of $0.05 < x < 0.225$. In addition to Ge⁴⁺, which has been mainly investigated for its ferroelectric characteristics, Ti⁴⁺ has been the most widely studied dopant in BIMEVOX [110]. Goodenough et al. [109, 129] observed that Bi₄V_{1.80}Ti_{0.20}O₁₁ is most promising composition for high conductivity. Yan et al. [111] have reported that the ionic conductivity increases with increasing Ti concentration up to x = 0.30 in Bi₄V₂O₁₁. It has the higher ionic conductivity ($\sigma = 4 \times 10^{-4} \text{ Scm}^{-1}$ at 225 °C) than other substitution in Bi₄V_{2-x}M_xO₁₁ (M⁴⁺= Zr, Sn, Pb, Ti). The ionic conductivity of x = 0.20

composition at 225 °C varies in the order of $\sigma(\text{Ti}) > \sigma(\text{Sn}) > \sigma(\text{Zr}) > \sigma(\text{Pb})$ in agreement with the trend of decreasing activation energy. The ionic conductivity of γ - $\text{Bi}_4\text{V}_{1.80}\text{Ti}_{0.20}\text{O}_{11}$ and γ - $\text{Bi}_4\text{V}_{1.80}\text{Cu}_{0.20}\text{O}_{11-\delta}$ measured by Yan et al. [111] are comparable to those reported by Krishnan et al. [110] on the same composition of BIMEVOX. However, the conductivities of γ - $\text{Bi}_4\text{V}_{1.7}\text{Ti}_{0.30}\text{O}_{10.85}$ are about one order of magnitude higher than that of γ - $\text{Bi}_4\text{V}_{1.80}\text{Cu}_{0.20}\text{O}_{11-\delta}$. They pointed out the importance of the defect pair formation on conductivities. These defect pairs are formed due to interaction between oxide ions vacancies [130]. Kant et al. [131] obtained highest conductivity in titanium doped $\text{Bi}_4\text{V}_{2-x}\text{Ti}_x\text{O}_{11-\delta}$ system for $x = 0.4$. In this system the value of conductivity observed is 24 times more than undoped sample at 300 °C. Microstructural features also support the highest conductivity of the titanium doped $\text{Bi}_4\text{V}_2\text{O}_{11}$ due to the optimum grain size (6-10 μm) which might be responsible for higher conductivity in this system. The samples of $\text{Bi}_4\text{V}_{1.6}\text{Ti}_{0.4}\text{O}_{11-\delta}$ have been further investigated to study the effect of sintering temperature. These samples were sintered at 750, 775, 800 and 825 °C. The conductivity of $\text{Bi}_4\text{V}_{1.6}\text{Ti}_{0.4}\text{O}_{11-\delta}$ sintered at 800 °C has been found to be highest than all other sintering temperatures. The highest conducting $\text{Bi}_4\text{V}_{1.6}\text{Ti}_{0.4}\text{O}_{11-\delta}$ 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. Hence titanium doped bismuth vanadate are found to be potential intermediate temperature electrolytes for IT-SOFC operation.

The chemical interaction studies of $\text{SrO-B}_2\text{O}_3\text{-SiO}_2\text{-La}_2\text{O}_3$ glasses with $\text{Bi}_4\text{V}_{1.8}\text{Al}_{0.2}\text{O}_{11-\delta}$ electrolyte have also been performed at 800 °C for different heat treatment durations [40]. During chemical interaction in all the samples SrVSi_2O_7 phase has formed. However, its volume fraction depends on the chemical nature of the modifiers used in glass and duration of heat treatment. Apart from SrVSi_2O_7 phase, AVO_4 and A_2SiO_5 ($A = \text{Y, La, Al, Bi}$) phases are also present in the glass electrolyte interaction product mass.

2.4 Gaps in the study

On the basis of above discussion, it can be concluded that the alkaline earth based glasses have shown quite promising results. However, the following are the noticeable points in these glass systems:

- ❖ Barium and strontium based glasses exhibit substantial chromate formation with chromia containing Crofer 22APU interconnect. Cr- containing ferritic steels are most widely used metallic interconnects due to their low cost and high oxidation resistance.

Chromium vaporizes at cell operating temperature and gets deposited at triple phase boundaries leading to degradation of SOFC stack performance.

- ❖ MgO based glasses are very prone to form cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) phase, which is detrimental due to their lower thermal expansion as compared to other components of SOFC.
- ❖ The compatibility of glasses with low-intermediate temperature electrolytes like bismuth vanadates has not been explored significantly. In addition to this, heat-treatment as a function of time to understand and gain insight into the interfacial diffusion phenomena is also less explored.

The interaction of glass sealants with different components of SOFC can also form different crystalline phases due to interdiffusion of anions and cations. Sometimes, these formed phases are very detrimental and cause deterioration of SOFC stack. However, the formation of detrimental phases can be avoided by suitably choosing the starting composition. Moreover, for implementing the glass seals to SOFC, seal properties such as flow, adhesion, CTE and chemical reactivity between glass and its surrounding components play a crucial role in determining the long-term reliability as well as structural integrity. Therefore, it is important and essential to understand the crystallization kinetics of glass seals during interaction with other components of SOFC.

2.5 Objectives

Based on these studies and also to address the existing gaps, following objectives have been planned for the present investigation:

- > To synthesize $\text{AO-B}_2\text{O}_3\text{-SiO}_2\text{-La}_2\text{O}_3$ (A= Mg, Ca, Sr, Ba) glass sealants.
- > To characterize these glasses for different thermodynamic parameters.
- > To make the diffusion couples of synthesized glasses with interconnect and electrolytes.
- > To study the chemical interaction of glasses with the interconnect (Crofer 22 APU) and electrolytes of the SOFC for different time durations.

In the present work, alumina free glasses have been chosen. Alkaline earth metal oxides reduce T_g and T_c , limits corrosion along with raising the CTE. MgO is also a crystallization inhibitor. La_2O_3 is a conditional glass former, which improves CTE and viscosity. Cations of SiO_2 and B_2O_3 units act as centers of polyhedral units and are basic network formers. B_2O_3 is a low

temperature glass former and a wetting agent. In addition to this, borate-containing species also attract attention due to their better thermodynamic and thermal stabilities.

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CHAPTER 3

EXPERIMENTAL TECHNIQUES

Overview

The detail of the experiment done for materials processing and characterization followed during the course of the present investigation, is presented in this chapter. Glasses and electrolytes were prepared using conventional melt-quenching techniques and solid-state reactions respectively. Differential thermal analysis/thermogravimetric analysis (DTA/TGA) and dilatometry were used for the measurement of thermal properties and characteristic parameters of prepared samples. X-ray diffraction (XRD) was used to confirm the amorphous nature of glass and to get information about the various phases formed during different heat-treatments. Scanning electron microscopy (SEM) was used for the microstructural analysis. In addition to this, electron probe microanalysis (EPMA) and X-ray dot mapping techniques were also used to know the concentration as well as segregation of elements. Two-probe method was used to measure the conductivity of solid electrolytes. Many optical techniques like Fourier-Transform Infra-red (FT-IR) spectroscopy, UV-Visible, Raman spectroscopy, Fourier-Transform nuclear magnetic resonance (FT-NMR) were also used to gain insight of glass structure and their structural properties.

3.1 Raw materials

The purity of constituent oxides, which were used to prepare the samples, was $\geq 99\%$. In the present study, raw materials used for preparing the samples were SiO_2 (99%, CDH), BaCO_3 (99%, Sdfine), B_2O_3 (99%, Sdfine), SrCO_3 (99% CDH), MgO (99% CDH), CaO (99% CDH), La_2O_3 (99.9%, CDH), Bi_2O_3 (99 % Sigma Aldrich), V_2O_5 (99% lobachemie), Ti_2O_3 (99.995% Sigma-Aldrich) and YSZ powder (TZ-8YS, Tosoh). Crofer 22APU (Thyssenkrupp VDM GmbH) was used as an interconnect. All these materials were used without any further purification.

3.2 Glass sample preparation

Glass samples were prepared by mixing the raw materials in the form of SiO_2 , B_2O_3 , La_2O_3 and SrO/MgO/BaO/CaO using conventional melt-quenching techniques. Each batch was prepared by mixing an appropriate mole fraction of well-desired initial ingredients. Sample compositions with their label are given in table 3.1.

Table 3.1: Glass compositions (mol %) with their labels.

Sample Label	SiO_2	B_2O_3	MgO	CaO	SrO	BaO	La_2O_3
ML	40	20	30	0	0	0	10
CL	40	20	0	30	0	0	10
SL	40	20	0	0	30	0	10
BL	40	20	0	0	0	30	10

For each system, required amount of raw materials as per the stoichiometry ratio were taken. The mixture was ground to break agglomerate particles. After grinding the mixture was further transferred to ball mill and ground for two hours in wet medium (acetone). The ball milling was done using porcelain balls in porcelain jar (Retsch, Germany, Model S 1000). The powder to ball ratio for each system was 1:2 which was kept constant for each milling. The resulting mixture was dried in air. The ground powder was transferred in recrystallized alumina crucible and melted in an automatized molybdenum disilicide (MoSi_2) high temperature furnace. The powders of the samples were initially heated at 1000°C for 2 h to facilitate the calcination. During calcination process gaseous substances (moisture + gas) are released. After that the temperature was increased upto 1200°C and kept at this temperature for 0.5 h to facilitate the fusion and melting process. Then, system was reheated at 1550°C and kept at this temperature

for 1.5 h to achieve homogeneous molten materials. The schedule followed for melting of samples is also shown in figure 3.1.

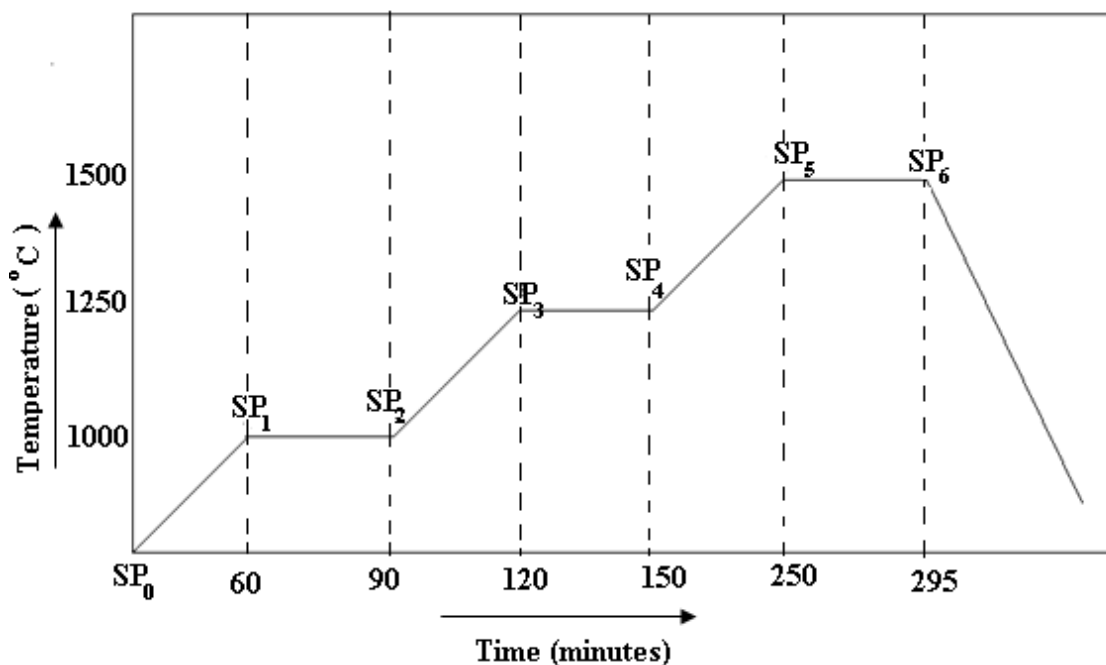


Figure 3.1: Typical schedule followed for the melting of the glass samples.

The molten mass was poured in a preheated graphite mold. The remaining melt was poured on the flat copper plate and quenched by other copper plate in air to obtain flakes. The obtained frits were annealed at 500 °C (below T_g , glass transition temperature) for 12 hours in air in a calibrated pit furnace. The annealing process is done to remove the internal stresses generated during quenching process. All the samples were prepared using the same route as described above. Before melting, the furnace was calibrated. The temperature gradient was ± 2 °C.

3.3 Electrolyte synthesis

In the present investigation, yttria stabilized zirconia (YSZ) and $\text{Bi}_2\text{V}_{1-x}\text{Ti}_x\text{O}_{5.5-\delta}$ ($0.05 \leq x \leq 0.25$) was used as high-temperature and intermediate temperature electrolytes, respectively. A high-purity YSZ powder (TZ-8YS, Tosoh) was used for making the pellets of dimensions 9 mm $\times$ 8 mm $\times$ 3mm (load of 12 kN/cm²) and sintered at 1450 °C for 12 h in high resistance furnace. Titania doped bismuth vanadate (TBV) i.e. $\text{Bi}_2\text{V}_{1-x}\text{Ti}_x\text{O}_{5.5-\delta}$ ($0.05 \leq x \leq 0.25$) powders were prepared by solid-state reaction from stoichiometric amounts of the following oxides: Bi_2O_3 (99.5%), V_2O_5 (99.5%) and Ti_2O_3 (99.5%). In order to avoid contamination due to ball milling, the mixing was done using agate mortar and pestle for 2 h in acetone media. The resulting

mixtures were dried, ground, and then calcined at 750 °C in recrystallized alumina crucible for 12 h in air. Calcined powders were again ground and pelletized by compacting these powders in hydraulic press at a load of 12 kN/cm². The pellets of 20 mm diameter and 5 mm thickness so prepared were sintered at 800 °C for 12 h.

3.4 Preparation of diffusion couple

The Crofer 22APU (Thyssenkrupp VDM GmbH) pieces were cut into 9mm × 8mm × 3mm dimensions. The composition of Crofer 22APU is given in table 3.2.

Table 3.2: Composition of Crofer 22APU interconnect in weight %.

Interconnect	Cr	Fe	Mn	Ti	C	S	P	Re
Crofer 22 APU	22.8	76.59	0.45	0.08	0.005	0.002	0.016	0.06

These pieces were ultrasonically cleaned in acetone. Two sets of the Crofer 22 APU/glass/Crofer 22APU diffusion couples were prepared using slurry technique. The glass powder was dispersed in ethanol and then deposited between Crofer plates to make sandwich like structure as shown in fig. 3.2.

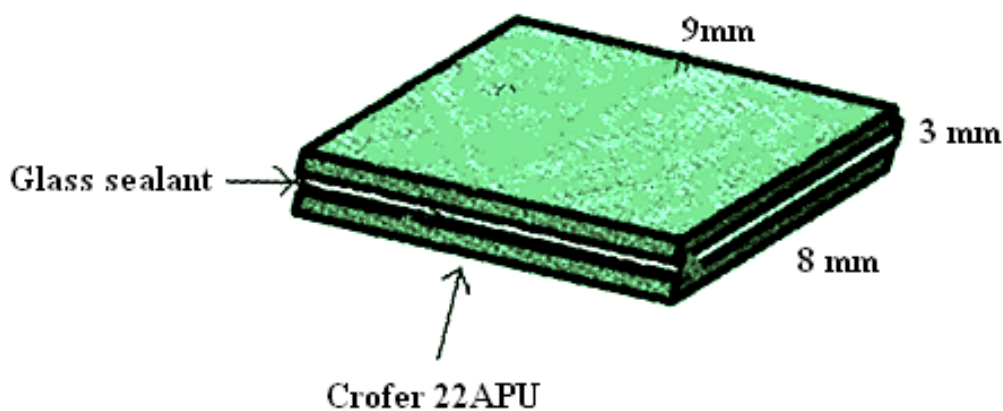


Figure 3.2: Diffusion couple of glass with Crofer 22APU.

Initially to make diffusion couple, the thermal treatment was given at 900 °C along with dwelling time of 30 mins to ensure incipient fusion of glass. The diffusion couples were heat-treated at 850 °C in tubular furnace for different durations of 5, 100 and 750 h. First set of heat-treated samples of diffusion couple were polished mechanically and etched with 5% HF. These

polished and etched diffusion couples were used for interfacial and microstructural analysis. From another set of diffusion couple glass seals were mechanically removed for checking the formation of different phases. Similarly, the diffusion couple of glasses with yttria stabilized zirconia (YSZ) and titania doped bismuth vanadate (TBV) electrolytes were prepared. While working with TBV, the heat-treatment temperature was kept at 800 °C. Mechanically removed coupled glass as shown below (fig. 3.3) was used for further investigation.

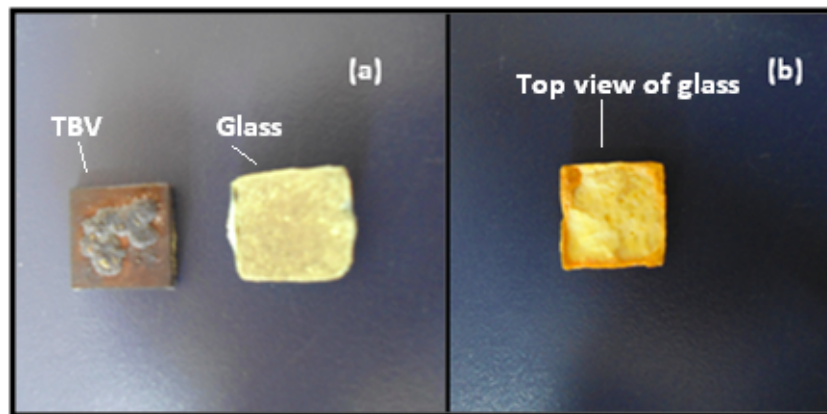


Figure 3.3 (a) Mechanical removed of ML glass from TBV (b) top view of removed glass.

3.5 Characterization of materials

The as prepared samples have been characterized using various techniques to know the initial and transformed structures during various heat-treatments as well as to check their applicability and suitability as sealing materials for SOFCs. The details of these techniques are given below:

3.5.1 X-ray diffraction

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed qualitative and quantitative information about the crystalline phases and crystallographic structure of natural and synthetic materials. X-ray powder diffraction pattern were recorded at room temperature using PANalytical X'perts PRO MPD diffractometer with CuK_α radiations ($\lambda = 1.5418 \text{ \AA}$). The XRD pattern are taken generally in the range of $10^\circ \leq 2\theta \leq 70^\circ$ for most of the samples at a scanning speed of $2^\circ / \text{min}$. Samples are analyzed as powders with grains in random orientations to insure that all crystallographic directions are sampled by the beam. Monochromatic X-rays are used to determine the interplanar spacing of the unknown samples using Bragg's law. The data obtained from XRD is indexed by standard powder diffraction files provided by International Centre for Diffraction Data –ICDD.

3.5.2 Density measurement

The density of glass samples was measured by Archimedes principle using microbalance with xylene as buoyant. Density data was used to calculate the molar volume (V_m) of as cast glasses using the following equation:

$$V_m = \frac{M}{\rho} \quad (3.1)$$

M denotes the molar mass of the investigated glass.

3.5.3 Differential thermal analysis (DTA) /Thermo-gravimetric analysis (TGA)

Differential thermal analysis (DTA) is a thermo analytical technique, similar to differential scanning calorimetry, which gives information about the phase transformation behavior of the sample. In DTA, the thermal event of sample is observed with respect to the inert reference sample in heating or cooling cycle under identical conditions. This differential temperature is then plotted against time, or against temperature (DTA curve). Changes in the sample, either exothermic or endothermic, can be detected relative to the inert reference. Thus, a DTA curve provides data on the transformations that have occurred, such as glass transitions, crystallization and melting. In the present work differential thermal analysis of the powdered samples was done by DTA, Perking Elmer (Diamond TG/DTA) in nitrogen atmosphere using platinum crucibles at different heating rates from room temperature to 1000 °C. In the present investigations Al_2O_3 is taken as reference sample. The endothermic peaks exhibit the glass transition temperature and melting of the glass samples. On the other hand exothermic peaks denote crystallization of the glasses. The thermal stability of the glasses was investigated using thermo gravimetric analysis (TGA). The temperature and weight loss detection limit are ± 1 °C and 0.001 mg, respectively during DTA/TGA measurements. The stability of glass at higher temperature can easily be predicted by TGA in terms of weight loss. B_2O_3 based glasses are known to be volatile at higher temperatures, the TGA can predict the degree of volatility in a particular glass accurately.

3.5.4 Dilatometric measurement

Thermal dilatometric analysis (TDA), often called "dilatometry", measures the dimensional change of a material (ceramics, glasses, metals, composites and others) as a function of temperature or time. This test determines both reversible and irreversible changes in length (expansion and shrinkage) during heating and cooling, and pinpoints the transition temperature

of expansion or contraction. The dilatometer is used to determine coefficient of thermal expansion (CTE), softening point, glass transition temperature, Curie point, crystalline transformation, phase transition, shrinkage, warping, bloating, sintering rate, isothermal creep and stress relaxation. If a temperature change from T_0 to T has caused expansion in a sample of initial length L_0 , the average coefficient of linear thermal expansion can be calculated as follows:

$$\alpha = (\Delta L_s / \Delta L_0) / (T - T_0) \quad (3.2)$$

This coefficient (α), often referred as CTE, is only true for the temperature range T_0 to T . In the present work dilatometry of the well-polished glass frits was done by dilatometer, Netzsch (DIL 402 PC) in air using alumina kit including alumina push rod. During the experiment the heating rate was 5 °C in oxidizing atmosphere and the temperature range was from room temperature to glass transition temperature. Thermographs have been taken between temperature and percentage change in length of the sample. Thermal expansion coefficient of all the glass samples was measured at various temperature ranges. Apart from glass CTE of doped bismuth vanadates (electrolyte) was also measured.

3.5.5 Scanning electron microscopy (SEM)

The scanning electron microscope (SEM) is a very powerful tool to study the morphological features of the samples using high-energy beam of electrons. The electrons interact with the samples and produce signals that contain information about the sample's surface topography, composition and morphology of crystalline phases. The types of signals that are produced by the SEM include secondary electrons (SE), back scattered electrons (BSE), characteristic X-rays, light (cathodoluminescence), specimen current and transmitted electrons. The detection of these signals requires specialized detectors for their detection that are located at different places in the machine. Scanning electron micrographs of polished, etched (with 5% HF) gold sputtered samples was recorded by SEM (EVO-ZEISS). The SEM was done either on fractured surface (for electrolytes) or on polished surface. In order to see the morphology of the phases present and to study the interaction between glasses and interconnect/electrolyte, SEM along with EPMA/X-ray dot mapping was done. To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of electrons is focused into the sample being studied. The incident beam excites an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills

the hole, and the difference in energy between the higher-energy shell and the lower energy shell is released in the form of characteristic X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy dispersive spectrometer. As the energy of the X-rays are characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they are emitted, this allows the elemental composition of the specimen to be measured.

3.5.6 Fourier transform infrared spectroscopy (FT-IR)

The term Fourier transform infrared spectroscopy (FT-IR) refers to a fairly recent development in the manner in which the data is collected and converted from an interference pattern to a spectrum. FT-IR is the preferred method of infrared spectroscopy in which IR radiation passes through the sample. Some of the infrared radiation is absorbed by the sample and some of it is transmitted. The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures can produce same infrared spectrum. FT-IR is also used to analyze the bonding of the samples. The wavelength of light absorbed is characteristic of the chemical bond. Fourier Transform Infra-red (FT-IR) spectroscopy was carried out at room temperature in the region $400\text{--}2250\text{ cm}^{-1}$ using Perkin Elmer Spectrum BX (2) spectrometer shown. The spectral resolution of FT-IR spectroscopy was $\pm 1\text{ cm}^{-1}$. 5 mg of each sample was mixed with 20 mg of KBr in an agate mortar and then this powder was used for recording the absorption spectra. The spectrum of each sample was normalized to the spectrum of the blank KBr.

3.5.7 UV- Visible spectroscopy

Ultraviolet-visible spectroscopy (UV/ VIS) involves the spectroscopy of photons in the UV-Visible region. It uses light in the visible and adjacent near ultraviolet (UV) and near infrared (NIR) ranges. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. UV-visible spectroscopy is the reliable and accurate procedure for analysis of samples absorption, transmission and emission of ultraviolet and visible wavelength by matter is measured. UV spectroscopy measures absorption and transmission of electromagnetic radiations by atoms or molecules. In present study, the optical transmission spectra of the glasses were recorded at room temperature using a double beam UV-VIS spectrophotometer (Model: Perkin Elmer 55) in the wavelength range of 200-800 nm. Methanol was taken as the reference solution. The spectrum of each sample was normalized to the spectrum of the blank

methanol. Subsequently the data was analyzed for calculating the band gap of the samples to know the effect of different oxides on the energy band gap of pristine samples.

3.5.8 Vicker's hardness

Micro hardness testing of metals, ceramics and composites is useful for a variety of applications. Micro hardness testing as per ASTM E-384 gives an allowable range of loads for testing with a diamond indenter and the resulting indentation is measured which is further converted to a hardness value. The actual indenters used are Vickers (more common; a square base diamond pyramid with an apical angle of 136°) or Knoop (a narrow rhombus shaped indenter). In the present investigation, Vickers micro-hardness tester (Mitutoyo, Japan) is used for measuring micro hardness of glass samples. The glass samples were mounted, grinded and polished. The Vickers micro-hardness is reported in kg/cm² and is proportional to the load divided by the square of the diagonal of the indentation measured from the test as given below:

$$HV = F/A \approx 1.8544F/d^2 \quad (3.3)$$

where F is kgf and d is millimeters.

3.5.9 Fourier transform nuclear magnetic resonance (FT-NMR)

The principle of NMR usually involves two sequential steps i.e. the alignment (polarization) of the magnetic nuclear spins in an applied, constant magnetic field H_0 and the perturbation of this alignment of the nuclear spins by employing an electro-magnetic, usually radio frequency (RF) pulse. The required perturbing frequency is dependent upon the static magnetic field (H_0) and the nuclei of observation. Non-zero spin is thus always associated with a non-zero magnetic moment (μ) via the relation $\mu = \gamma S$, where γ is the gyromagnetic ratio. It is this magnetic moment that allows the observation of NMR absorption spectra caused by transitions between nuclear spin levels. Thus, ¹⁸O is an example of a nuclide that has no NMR absorption, whereas ¹³C, ¹⁵P, ³⁵Cl and ³⁷Cl are nuclides that do exhibit NMR absorption spectra. The last two nuclei are quadrupolar nuclei whereas the preceding two nuclei (¹³C and ¹⁵P) are dipolar ones. In order to obtain the frequency-domain NMR spectrum (NMR absorption intensity vs. NMR frequency) the time-domain signal (intensity vs. time) must be Fourier transformed. In the present study, Fourier transform-nuclear magnetic resonance (FT-NMR) spectra of glasses were recorded on a Bruker Avance-II (400 MHz) spectrophotometer. Dispersion of glass in methanol was made. Methanol was taken as the reference solution and the spectrum of each sample was normalized to the spectrum of the blank methanol.

3.5.10 Raman spectroscopy

Raman spectroscopy is a spectroscopic technique used to study vibrational, rotational, and other low-frequency modes in a system. Raman spectroscopy is commonly used, to observe vibrational information, which is specific to the chemical bonds and symmetry of molecules. It therefore provides a fingerprint by which the molecule can be identified. Raman scattering is an example of inelastic scattering because of the energy transfer between the photons and the molecules during their interaction. Typically, a sample is illuminated with a laser beam. Light from the illuminated spot is collected with a lens and sent through a monochromator. The laser light interacts with phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. A change in the molecular polarization potential or amount of deformation of the electron cloud with respect to the vibrational coordinate is required for a molecule to exhibit a Raman effect. The shift in energy gives information about the phonon modes in the system. Wavelengths close to the laser line, due to elastic Rayleigh scattering, are filtered out while the rest of the collected light is dispersed onto a detector. Raman spectra of pristine glass powders were recorded using Renishaw in Via Raman spectrometer with 514 nm He Ne laser.

3.5.11 A.C. Conductivity

Impedance spectroscopy is a powerful ac measurement technique, which has been applied quite successfully to determine a number of important characteristics such as bulk resistivity in case of single crystals and contribution of grain and grain boundary resistance in polycrystalline solid electrolytes. Interface between the electrode and sample electrolyte therefore adds a double-layer capacitance in series with the simple bulk resistance and with the resistance due to grain boundary effects. In the case of parallel combination of R and C, as shown in fig 3.4 (a),

$$Z = \left(\frac{1}{R} + i\omega C \right)^{-1} = \frac{R}{1 + (\omega RC)^2} - R \frac{i\omega RC}{1 + (\omega RC)^2} \quad (3.4)$$

The data when plotted lies in a semicircle in the complex Z^* plane, as shown in fig. 3.4 (b). A simple equivalent circuit model that could be used to represent electrode-electrolyte system consists of three parallel RC circuits representing grain, grain boundaries and electrodes, connected in series.

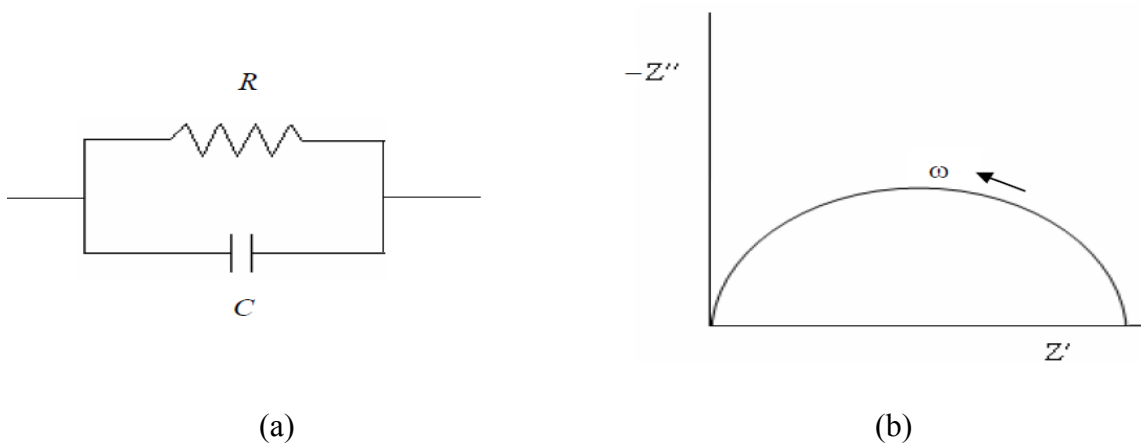


Figure 3.4: (a) Parallel combination of R and C (b) Impedance plot.

The values of the components are obtained from the intercepts of respective arcs on the Z' axis and the frequencies at which the arcs show a maximum height. Thus the values of resistivities can be obtained from ac measurements. In the present study, ionic conductivity was measured by an ac impedance analyzer with multi frequency Hewlett-Packard LCR meter (Model 4274A) in the frequency range of 100 – 100 kHz. The gold sputtered (Ion sputter-JFC, model 1100) pellets were used to carry out a.c. conductivity measurement in the temperature range of 200 to 700 °C during cooling cycle.

CHAPTER 4

RESULTS AND DISCUSSION-I

Overview

In the present study, major focus is on the chemical compatibility of RO-B₂O₃-SiO₂-La₂O₃ [R = Mg, Ca, Sr, Ba] glass seals with Crofer 22 APU metallic interconnect as a function of different heating durations to understand the mechanisms of interfacial interaction. The diffusion couples of glass/ Crofer 22APU were made using slurry technique. The diffusion couples were heat-treated for different durations and then investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), electron-probe microanalysis (EPMA) and X-ray dot mapping techniques. It is essential to study thermal, mechanical and band gap properties of glasses so that structure-properties correlation could be established before using them for interaction study. The properties of glasses were investigated using UV-VIS, FTIR spectroscopy, Raman spectroscopy, Nuclear magnetic resonance (NMR), Dilatometer and Vicker's microhardness tester. Furthermore, hardness and indentation toughness of glasses are analysed using the statistical aspect. To gain insight into crystallization mechanism, various thermodynamic parameters like Lasocka parameter, activation energy of crystallization, frequency factor, crystallization constants and Avrami parameter have been evaluated using differential thermal analysis (DTA).

4.1 Physical properties of glasses

4.1.1 Density and molar volume

The densities along with ionic concentration of alkaline earth ions, inter-ionic distance and molar volume of the glasses are given in table 4.1. The densities of all the as prepared glasses are measured by Archimedes principle. The molar volume of the glass is calculated using following relation:

$$V_m = M/\rho \quad (4.1)$$

where M is molecular weight and ρ is density of glass. Ionic concentration of alkaline earth metal ions (N) and their inter-ionic distance (R) are calculated using following relation:

$$N = (6.023 \times \text{mol\% of cation} \times \text{valency}) / V_m \quad (4.2)$$

$$R = (1/N)^{1/3} \quad (4.3)$$

Table 4.1: The densities, molar volume of the glasses, ionic concentration of alkaline earth ions and their inter-ionic distance.

Glass	Density, ρ (g/cm ³)	Molar volume, V_m (cm ³ /mol)	Ionic conc. , $N(\times 10^{21}/\text{cm}^3)$	Inter-ionic distance, R (Å)
ML	3.32	23.81	15.17	4.04
CL	3.67	24.90	14.51	4.09
SL	3.69	27.55	13.11	4.23
BL	3.89	29.97	12.07	4.34

BL glass is having highest density, which is due to higher atomic weight of Ba²⁺. Additionally higher value of molar volume for BL glass indicates less cross-linking within the glass matrix. Ionic concentration is highest for Mg²⁺ whereas its inter-ionic distance is lowest in all the glasses. This may be attributed to its small ionic radii as compared to other glass modifiers [1]. So the addition of network modifier do not contribute in glass formation but cleaves the structure of glass network and causes an increase in the molar volume of the glass. The results obtained for the present glass system are in good agreement with those reported for semiconducting glasses. The local glass structure can be created as shown in fig. 4.1. Tetrahedral coordination occurs for silica as well as boron. Lanthanum in the local network may occupy interstitial octahedral sites. The modifier breaks the B-O or Si-O bonds and occupies interstitial or substitutional position in glass network. The glass network consists of BO₃, BO₄, SiO₄ units along with LaO₆ octahedral ring.

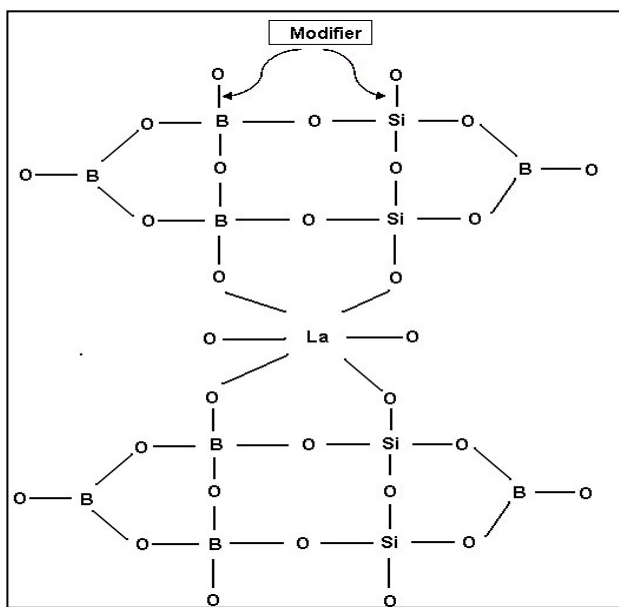


Figure 4.1: The anticipated structure of glass network.

4.2 Structural analysis

4.2.1 X-ray diffraction

X- ray diffraction patterns of all glasses are shown in fig. 4.2. The absence of Bragg's diffraction peaks clearly indicates the absence of crystalline phases. All the as-prepared glasses exhibit broad halo at low angles $\approx 27^\circ$ for the glass samples. This confirms their complete amorphous nature as well as absence of long-range disorder.

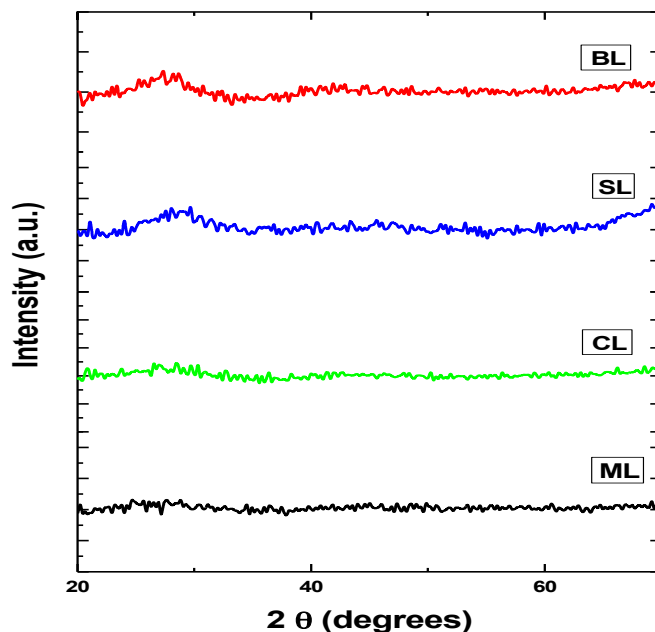


Figure 4.2: The XRD diffractogram of all pristine glasses.

4.2.2 Fourier transform infrared analysis (FT-IR)

The FT-IR spectra of glass samples are shown in fig. 4.3. It exhibits very small absorption band at $650\text{--}780\text{ cm}^{-1}$, which can be assigned to Si-O-Si symmetric stretching of bridging oxygen between tetrahedra. Additionally, strong absorption band appeared at 888 cm^{-1} which can be attributed to Si-O⁻ stretching with two non-bridging oxygen [2]. Apart from these bands, FT-IR spectra also exhibit weak band variation at 1604 cm^{-1} . These variations can be assigned to H₂O molecular vibrations. The small kinks at 1198 cm^{-1} could be assigned to Si-O-Si asymmetric stretching of bridging oxygen. The small kinks at 1487 and 1507 cm^{-1} are observed which can be due to B-O vibrations of various borate groups [3-4]. All the glass samples clearly indicate the presence of B-O and Si-O-Si functional groups in their FTIR spectra.

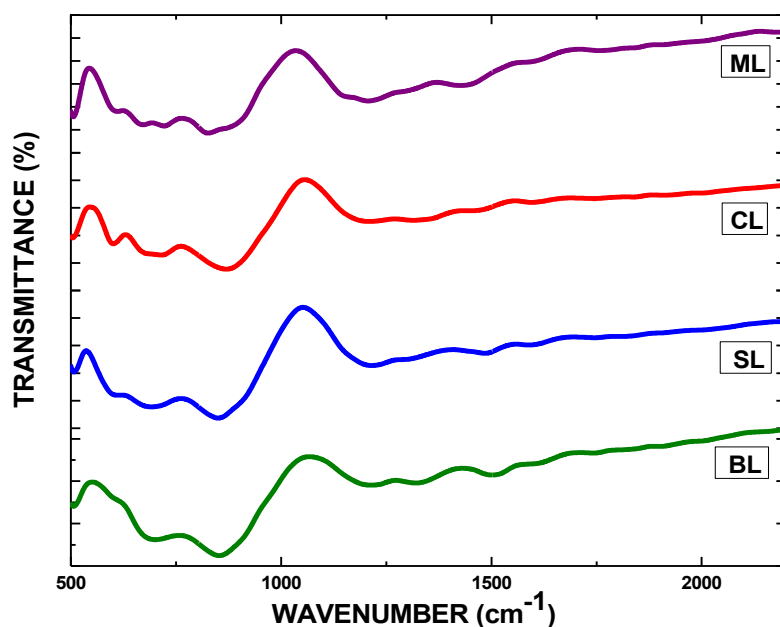


Figure 4.3: FT-IR spectra of all pristine glass samples.

It is well-established fact that addition of heavy cations in glass shifts the peaks to lower wave numbers [2-3]. With the introduction of heavier cation, the structural rearrangement can take place in Si-O-Si environment leading to strained network and hence resulting in distortion of local symmetry. The small shifting of FT-IR bands to the lower wavenumber side is observed in glasses as the modifier is changed from MgO to BaO. According to Central Force Model, the shifting of Si-O-Si stretching vibrational frequency can be due to the structural changes which are associated with variation of inter tetrahedral Si-O-Si bond angles [5]. The band at 736 cm^{-1} is getting broadened indicating the scission of Si-O-Si chain in the glass network. The bands

centered at 873 and 896 cm^{-1} is assigned to the Si-O⁻ stretching with two non-bridging oxygen per SiO₄ tetrahedron. These bands are becoming stronger with the replacement of heavy modifier as it is breaking the network structure of glass former, thus producing non-bridging oxygens (NBO's) with the gradual incorporation of ions in the glass structure. When alkaline earth metal ions occupy interstitial position, then it can introduce coordinated defects known as dangling [6].

4.2.3 Raman spectra

The Raman spectra of all the glasses are given in fig. 4.4.

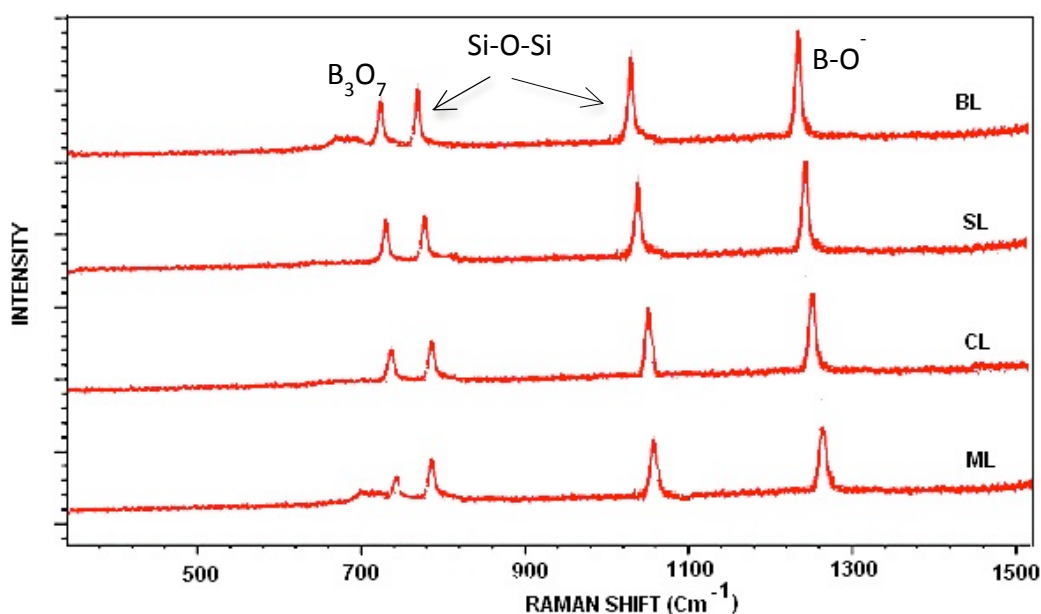


Figure 4.4: Raman spectra for all the glass samples.

Observed Raman features (RF) in present case can be classified as follows:

(1) The responses which are observed due to borate network occur at around 770-779 cm^{-1} and 1274-1280 cm^{-1} . RF at around 770-779 cm^{-1} can be assigned to the out of plane bending of triborate group [B₃O₇] [7]. The strong RF observed at around 1274-1280 cm^{-1} can be attributed to network composed of boroxol and also by B-O⁻bonds which are attached to large borate groups [8]. An increase in intensity of these RF occurs in the order $\text{RF}_{\text{BL}} > \text{RF}_{\text{SL}} > \text{RF}_{\text{CL}} > \text{RF}_{\text{ML}}$ which can be attributed to increase in number of boroxol rings and triborate groups. It indicates that with introduction of heavy modifier cations, the number of NBO's increases, thus enhancing network disorder. These results are also supported by the FT-IR spectra of these glasses.

(2) The major features due to silicate network vibrational modes occur at $796\text{--}800\text{ cm}^{-1}$ and $1060\text{--}1070\text{ cm}^{-1}$. The peaks at $796\text{--}800\text{ cm}^{-1}$ are associated with symmetric Si-O-Si stretching or vibrational modes of ring structures [9]. The strong RF observed between $1060\text{--}1070\text{ cm}^{-1}$ is assigned to Si-O-Si asymmetric stretching mode [10]. Similar trend of intensity is also observed for silicate network. Raman features observed in the present study gives two important results i.e. the number of NBO's increases and shifting of all bands towards lower wavenumber is observed with replacement of heavier modifier atoms.

4.2.4 FT-nuclear magnetic resonance

The NMR spectra of glasses exhibit two resonant absorption peaks for ^{11}B as shown in fig. 4.5(a). One absorption line is centered between -1 to -1.5 ppm which arises from boron atoms in oxygen tetrahedron (BO_4 units). Boron atoms of boroxyl structural groups [BO_3 units] yield relatively sharp peak near -2 ppm [11]. The centre of gravity of peaks shift from -1.13 to -1.43 for BO_4 units as the magnesium is replaced by barium cation.

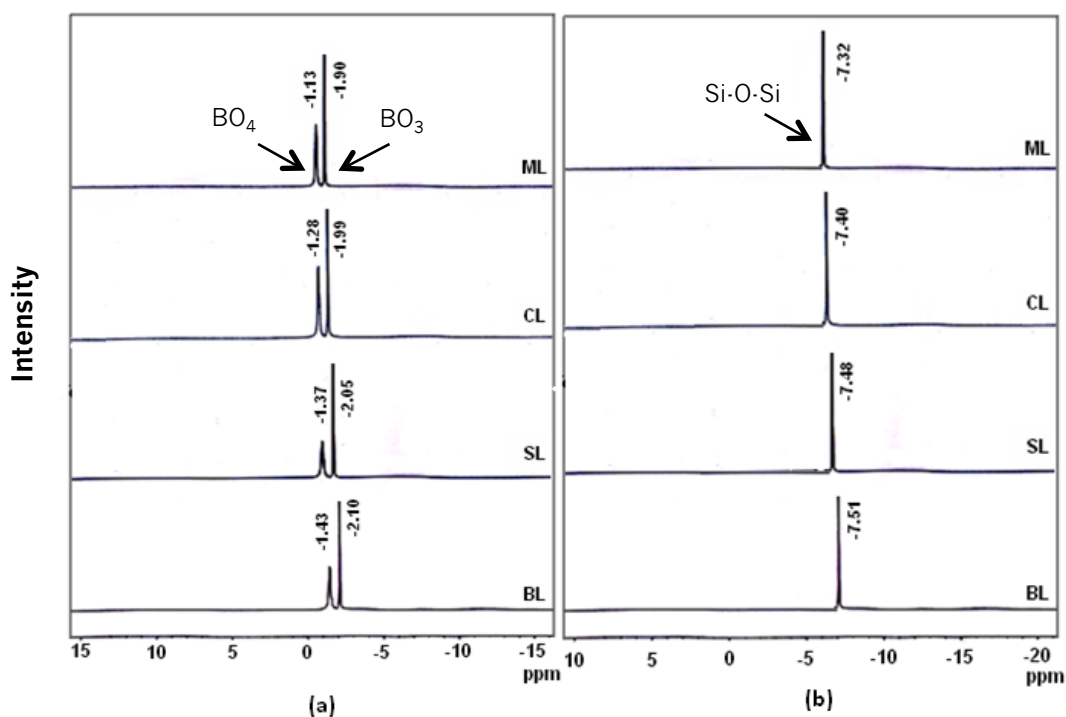


Figure 4.5: (a) FT-NMR (^{11}B) and (b) FT-NMR (^{29}Si) of all the glasses.

Similarly, the center of gravity of BO_3 unit shifts from -1.90 to -2.10 . The BO_4 peak is fairly broad which is signature of existence of variety of BO_4 species in the present glasses [12]. Triangulated boron species exhibit four main types of structural units i.e. T^3 group posses three

oxygen bridging to other network formers, T^2 group have one NBO and two bridging oxygens (BO's), T^1 have two NBO's and one BO, and T^0 possesses three NBO's. Among these units, T^0 and T^3 have symmetrical triangular units whereas T^1 and T^2 have asymmetrical triangular arrangements [13]. Both the arrangements have structurally different shapes. Single strong absorption peak is present between -7.30 to -7.55 and these values indicate the presence of Q^2 -type silica tetrahedra in the glass network as shown in fig. 4.5 (b) [14]. In the case of ^{29}Si NMR spectra also, shift of centre of gravity has been observed from -7.32 to -7.51 ppm with change of heavy modifier cations. These results clearly indicate an increase in NBO containing structural units in the glass network, when modifiers are replaced in order of Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} in the glasses.

4.3 Band-gap measurements

4.3.1 UV-VIS Spectroscopy

As given in chapter 1, the sealing materials should have higher electrical resistance. The band gap measurements gives fair idea about these properties. According to Tauc, the variation of absorption coefficient with photon energy shows three regions in many amorphous materials. The first region corresponds to 'Tauc region' which is for to high absorption from which optical energy band can be calculated. This region is associated with inter band transitions i.e. it may correspond to transition of an electron belonging to an ion in an excited state [15]. As a consequence of this, a sharp increase in the absorption coefficient $\alpha(\nu)$ will result. The more weakly these electrons are bound, the more easily absorption occurs. For Tauc's region, the absorption coefficient is given in quadratic form, which is discussed, by Mott and Davis [16] in more generalized way:

$$\alpha h\nu = \text{const} [(h\nu - E_{\text{opt}})^n / h\nu] \quad (4.4)$$

where $h\nu$ is the photon energy and E_{opt} is the optical band. Here, n is an index that has different values depending on the mechanism of inter-band transitions i.e. 2, 3, 1/2, 1/3 values corresponding to indirect allowed, indirect forbidden, direct allowed and direct forbidden. E_{opt} values are determined from the curves representing $(\alpha h\nu)^2$ as a function of extrapolation of linear region of the plots of $(\alpha h\nu)^{1/2} = 0$ as shown in fig. 4.6. The values of E_{opt} are listed in table 4.2. It can be seen that the band gap decreases from 2.84 to 2.02 eV as modifier is replaced from Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} . Its introduction would cause the Si-O-Si bonds breakage and creates appearance of NBO's in the glass network. Shift of energy gap to lower energies can be due to

the formation of NBO's. Moreover, the negative charge on NBO's has higher magnitude than BO. When the ionicity of oxygen atoms is increased by converting them from bridging to non-bridging, then the top of valence band is raised resulting in reduced energy gap [17].

Table 4.2: Band gap and urbach energy of all glass samples.

Glass Sample	E_{opt} (eV) ± 0.01	E_u (eV) ± 0.01
ML	2.82	0.34
CL	2.42	0.39
SL	2.21	0.43
BL	2.02	0.47

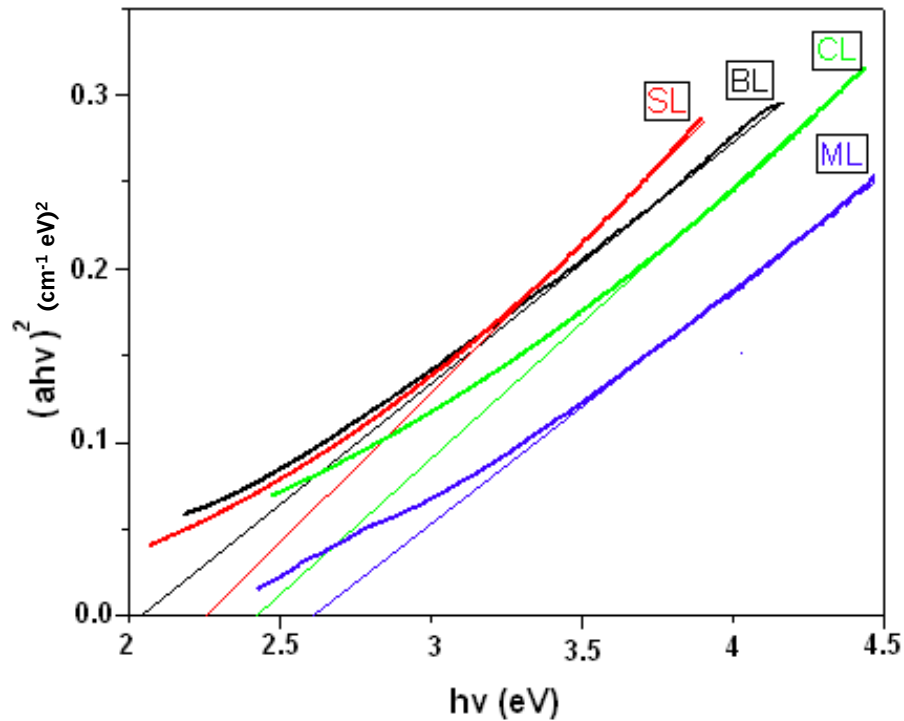


Figure 4.6: Band gap for all the glass samples.

It is well reported in the literature that the introduction of heavy metals like barium in glass composition decreases the optical band gap [18]. The change in optical band gap is also attributed to the structural changes due to occupancy at different sites by cations. The second region known as ‘Urbach region’ is exponential region due to the randomness and structural disorientations of the system. Disordered materials produce localized states in the band gap which results from exponential absorption tail. For small absorption coefficients ($\alpha < 10^{-4} \text{ cm}^{-1}$),

there is usually an Urbach tail where $\alpha(\nu)$ depends exponentially on the photon energy $h\nu$ as follows :

$$\alpha(\nu) = \alpha_0 \exp (h\nu/E_u) \quad (4.5)$$

where α_0 is the constant and E_u is Urbach energy which is the width of the tails of localized states in the band gap representing degree of disorder in amorphous materials. E_u values are calculated from slopes of linear portion of the curve between $\ln(\alpha)$ against $h\nu$ and are listed in table 4.2. The exponential dependence of $\alpha(\nu)$ on photon energy depicts that the material obeys Urbach rule. Dow and Redfield [19] described the cause of Urbach energy as the random internal electric field associated with the structural disorder, which broadens the excitons line. Tauc and Menth [20] have reported that disordering can arise from transitions between the localized states in the band edge tails where the density is assumed to fall exponentially. Many factors like dislocations, thermal vibrations and electric field of defects etc. can cause the tailing of energy states in the forbidden gap. The increase in Urbach energy with the replacement of higher atomic number modifier again suggest that there is an increase in amorphousness as well as open structure of the glass due to the formation of more non-bridging oxygen. The third region is the weak absorption tail produced from defects and impurities in UV spectra.

4.3.2 Determination of the refractive index

According to the theory of reflectivity of light, the refractive index n , as a function of the transmission measurements is determined by the quadratic equation [21]:

$$n = [1 + (1-T^2)^{1/2}]/T \quad (4.6)$$

It is clear from the fig. 4.7 that the refractive index decreases with an increase in the wavelength of the incident photon. For BL glass, maximum refractive index is obtained. The variation of refractive index can be explained on the basis of Lorentz-Lorenz equation as follows [21]:

- (1) Refractive index varies directly in accordance with the density.
- (2) Co-ordination number also affects the refractive index. BaO is strong modifier in comparison to MgO, CaO and SrO. It creates more NBO's which in turn increases the average co-ordination number of glasses.
- (3) Increase in NBO's leads to creation of more ionic bonds at the cost of covalent bond. This further gives larger polarizability values (discussed in next section), hence increasing the refractive index values.

As described by Baki et al. [22], every added alkaline earth metal ion (A^{2+}) provides extra oxygen to network, eliminating bridging oxygen and creating NBO's as follows:

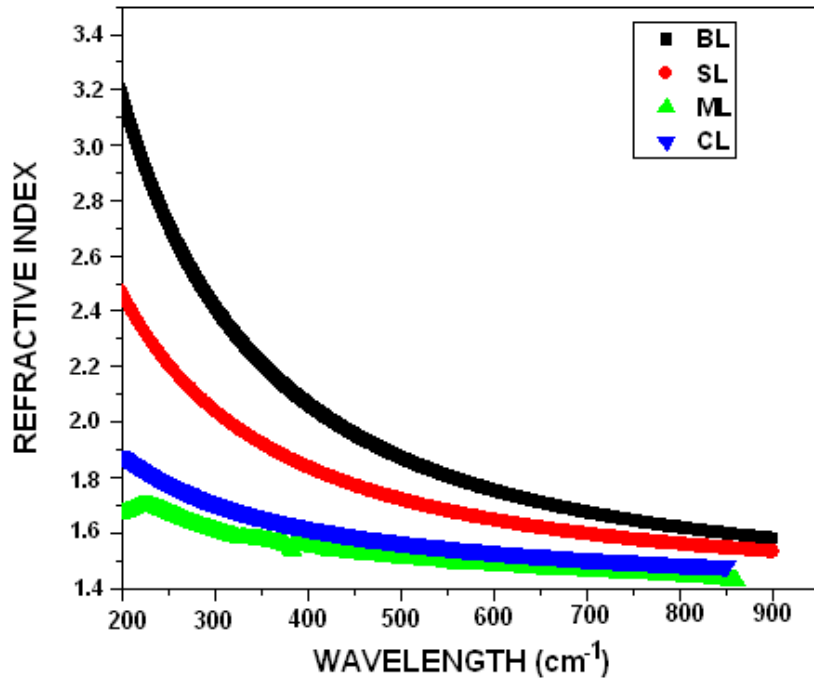


Figure 4.7: Variation of refractive index with wavelength of various glass samples.

A^{2+} ions will act partly as bridges between network forming groups and partly enclosed within the structural interstices, which is known as ionic bridging position. This position is least stable position [22]. These divalent cations can also act as bridges between adjacent BO_4 tetrahedron. When the divalent cations are replaced in the following order Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} , then the oxygen atoms around these cations become weakly held and hence get strongly polarized. This can be interpreted to an increase in refractive index. Consequently, refractive index is expected to vary in accordance $BL > SL > CL > ML$ glasses, which is in complete agreement with the other experimentally obtained results of the present study.

4.3.3 Optical Basicity

Optical basicity (Λ_m) can be used as a measurement of acid-base properties of oxide glasses. The oxygen atoms in glass behave as Lewis bases because they transfer a part of their negative charge to cations. In general, this tendency increases with increasing NBO's in glass system

[23]. Increasing basicity results in increasing charge on oxygen which further increases the covalency of cation-oxygen bond. According to Duffy [24]:

$$x_o - x_m = \sqrt{[(Q+1.13)/2b]} \quad (4.8)$$

where 2b is the number of bonds, Q is the heat of formation (in kJ/mol), x_o and x_m are the electronegativity values of oxygen ions and metal ions, respectively. These values are summarized in table 4.3.

Table 4.3: The metal ion electronegativity (x_m), oxide ion electronegativity (x_o), basicity moderating parameter (γ_m) and optical basicity of individual oxides (Λ_o).

Oxides	x_m	x_o	γ_m	$\Lambda_o \pm 0.01$
MgO	1.20	3.12	1.28	0.78
CaO	1.00	2.96	1.00	1.00
SrO	0.95	2.86	0.91	1.09
BaO	0.90	2.75	0.87	1.15
B ₂ O ₃	2.00	3.66	2.36	0.42
SiO ₂	1.80	3.51	2.08	0.48
La ₂ O ₃	1.10	2.71	1.13	0.88

The variation of x_o with respect to x_m is shown in fig.4.8. The optical basicity can be calculated from chemical composition using following relation [25]:

$$\Lambda_m = \sum O_i / O \gamma_m \quad (4.9)$$

O is the total number of oxygen atoms present, γ_m is the basicity moderating parameter and O_i is number of atoms in individual oxides. Basicity moderating parameter is almost similar to electronegativity as both parameters measure the attraction of electrons for chemical bonding. The optical basicity of the ML, CL, SL and BL glass samples is 0.57, 0.60, 0.62 and 0.63 respectively. BL sample has highest value of optical basicity due to higher number of NBO's in this glass and lowest field strength in the present glasses. The field strength(charge/radius ratio) associated with divalent alkaline-earth metal ions Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} varies as 0.45 , 0.33, 0.30 and 0.24, respectively [26]. For a single oxide, basicity Λ_o is given by the reciprocal of the basicity moderating parameter and are listed in table 4.4 for all the oxides. Field strength plays very important role to strengthen the glass network via bonding to neighbouring oxygen. The Ba^{2+} having the highest cationic radius (corresponding to smallest field strength), experiences less attraction from the non-bridging oxygen. Although Ba^{2+} forms more co-

ordinate links, it does not sufficiently reinforce the structure due to its linkage with the non-bridging oxygen. Therefore, BL samples, having BaO as modifier, has higher values of optical basicity. The increasing thermodynamic stability is associated with increasing charge on oxygen atoms. The distribution of bulk optical density Λ_m in the glass changes as the network disrupts. It depends on whether the oxide is bridging or non-bridging as well as the co-ordination of ions.

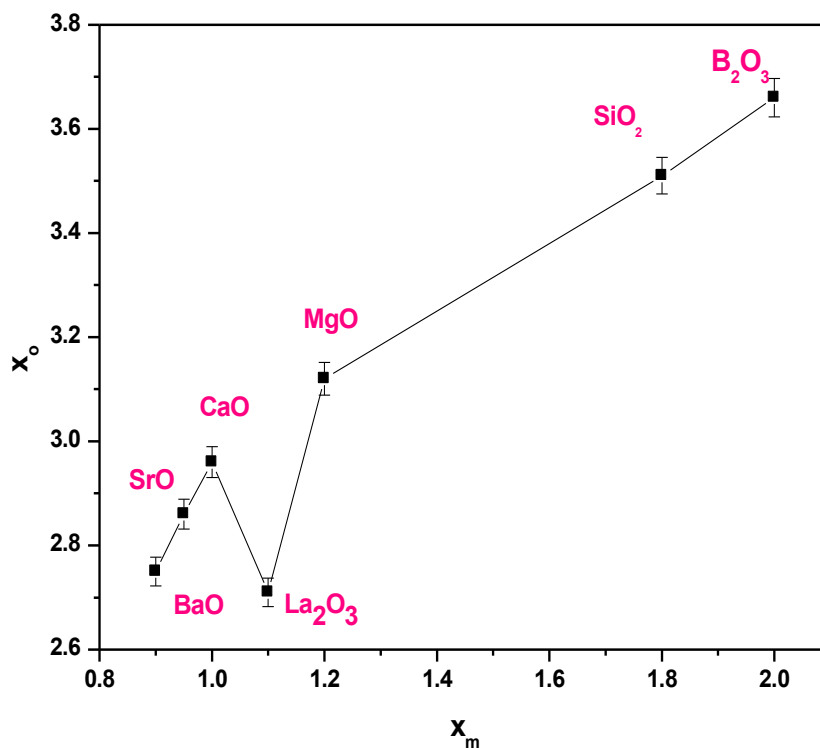


Figure 4.8: Variation of metal-ion electronegativity and oxygen electronegativity of constituents of glasses.

Therefore, microscopic optical basicities (σ) are assigned to the individual oxides although the bulk optical density, Λ_m remains unchanged [27]. The general equation for the calculation of σ of an oxide medium is given by:

$$\sigma = 1 - [(z_a r_a / 2) (1 - 1/\gamma_a) + (z_b r_b / 2) (1 - 1/\gamma_b) + \dots] \quad (4.10)$$

where z_a , z_b are the oxidation numbers, γ_a and γ_b are basicity moderating parameters, r_a and r_b are the ratios of cations with respect to total number of oxides. To calculate the microscopic optical basicity of single oxide e.g. for borate glass, we can employ following relation:

$$\sigma = 1 - (3r_a/2) (1-1/2.36) = 1 - 0.864 r_a \quad (4.11)$$

r_a depends upon coordination of boron. Similarly, for all other oxides the microscopic optical basicity have been calculated and summarized in table 4.4. It is observed that the σ is higher for non-bridging oxides. This clearly implies that non-bridging oxides are much more basic than bridging oxides. This further leads to the formation of basic sites inside the structure. Moreover, the σ follows the order $\text{BaO} > \text{SrO} > \text{CaO} > \text{MgO}$ which clearly indicates that the basic character increases down the alkaline earth group.

Table 4.4: Microscopic optical basicities (σ) for bridging as well as non-bridging oxides.

Co-ordination Oxide ∇	Bridging (σ)			Non-bridging (σ)	
	Threefold	Fourfold	Threefold/Fourfold	Threefold	Fourfold
B_2O_3	0.57	0.50	0.42	0.71	0.78
SiO_2	0.48	0.39	0.31	0.65	0.74
La_2O_3	0.88	0.91	0.89	0.94	0.97
MgO	0.85	0.89	0.87	0.93	0.94
CaO	1.00	1.00	1.00	1.00	1.00
SrO	1.05	1.07	1.06	1.08	1.09
BaO	1.08	1.10	1.09	1.11	1.14

4.3.4 Oxide ion polarizability

Electronic polarizability of oxide ions (α_o) has strong intrinsic relationship with the optical basicity of oxide ion. Increase in oxide ion polarizability indicates stronger electron donating capability of oxide ions. According to Fajan rule [28], high electronic polarizability means small anion and large cation or vice-versa. Duffy [23] proposed an approach for the calculation of state of polarization of oxide ions in glass matrix. For the optical basicity range of 0.35 - 0.75 including the oxides of SiO_2 and B_2O_3 , α_o is given as follows:

$$\alpha_o = [(1.567 \Lambda_m + 0.362)^2 + 2.868] / 3.133 \quad (4.12)$$

According to eq. (4.12), an increase in optical basicity increases the polarizability. The α_o values calculated are 1.59, 1.64, 1.66 and 1.68 for ML, CL, SL and BL glass, respectively. Lowest value of polarizability for ML glass indicates its poor electron donating capacity. As the ionic radii of modifier ion increases in order $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$, the α_o is observed to increase which goes in accordance to Fajan's rule. This indicates that the oxide ions are weakly polarized in ML glass and strongly polarized in BL glass. Highest polarizing power of BL glasses is responsible for its high refractive index as observed from fig. 4.7.

4.4 Mechanical properties of glasses

4.4.1 Micro hardness testing and cumulative distribution function

The Vicker's hardness and indentation fracture toughness of all the glasses is summarized in table 4.5. Hardness of the glasses has been calculated using following equation [29]:

$$H = F/A \approx 1.8544F/d^2 \quad (4.13)$$

where F is load (kgf) and d is diagonal length of indentation. The fracture toughness (K) is measured using the relevant solution for Anstis equation [30]:

$$K = 0.016 (E/H)^{1/2} (F/c^{3/2}) \quad (4.14)$$

Where F is the indentation load, c is the half-length of the resultant indentation cracks, E and H are the Young's modulus and the hardness of the test materials, respectively. An elastic modulus (E) of 200 GPa is used for calculating fracture toughness [31]. It can be observed that ML sample has maximum hardness as well as fracture toughness. The reason can be attributed to the bond strength pattern which varies as $MgO > CaO > SrO > BaO$ [32]. ML sample has greater bond strength and hence much attraction between bonds. Due to this, ML glass exhibits higher hardness than other three glasses.

Table 4.5: Hardness, fracture toughness and Weibull parameters for all glass samples.

Glass	Hardness, H (GPa) ± 0.05	Fracture toughness, K (MPa m ^{1/2}) ± 0.05	Weibull parameters	
			K _o (MPa m ^{1/2}) ± 0.01	m ± 0.01
ML	5.21	1.22	1.16	14.11
CL	4.54	1.05	0.98	11.93
SL	4.11	0.94	0.91	14.91
BL	3.65	0.87	0.83	18.53

In addition to this, the cumulative distribution function for normalized K of present glasses has been calculated. 50 K data are calculated for each glass and then normalized by their average value (K_{av}). The obtained values are then arranged from lowest to highest. Cumulative probability of failure, P_i is assigned to the i^{th} result of $(K_c/K_{av})_i$ as given by Gong [33]:

$$P_i = (i - 0.5)/50 \quad (4.15)$$

The shape of the CDF obtained in fig. 4.9 is in correlation with those generally observed for the brittle ceramics. The Weibull statistics [34] is commonly used to describe the fracture behavior of brittle materials. According to weakest-link hypothesis, it is assumed that the most severe

flaw controls the strength of the materials. Under an applied stress K , the cumulative probability of failure for a brittle material can be expressed as:

$$P_i = 1 - \exp \left[-\left\{ \frac{(K - K_u)}{K_o} \right\}^m \right] \quad (4.16)$$

where K_o is the Weibull characteristic strength, K_u is the threshold stress below which no failure will occur, and m is the Weibull modulus.

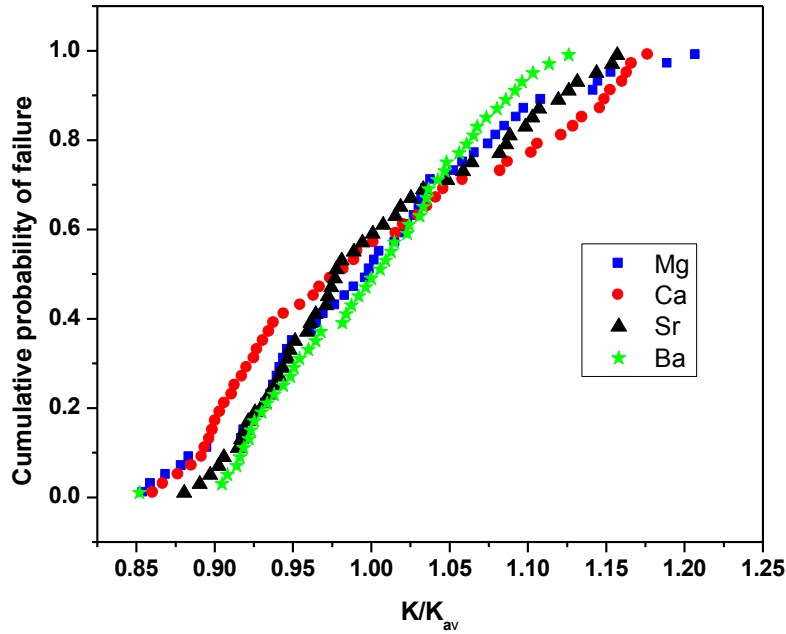


Figure 4.9: Cumulative distribution function for normalized toughness of all the glasses.

Weibull modulus m is a measure of the degree of strength data dispersion. Mostly K_o is assumed to be zero, then eqn. 16 can be written as [34]

$$P_i = 1 - \exp \left[-\left(\frac{K}{K_o} \right)^m \right] \quad (4.17)$$

Now, Weibull probabilistic equation has two parameters which can be easily applied to analyze the scattering of the strength data generated for the current study. 50 data points for Weibull analysis have been generated for each glass and are depicted in fig. 4.10. K_o and m are estimated with the conventional least-square fitting method. The obtained results are summarized in table 4.5. The characteristic Weibull strength K_o is highest for ML glass, which can be due to its high bond-strength. Weibull modulus is highest for BL sample and low for CL glass indicating high data dispersion in BL sample. This is in correlation with obtained values of hardness and fracture toughness for the present samples. The above study clearly indicates that

modifiers influence the basic property of glasses. This is because of variation in their field strength, which ultimately influences the local arrangements of the ions in glass matrix.

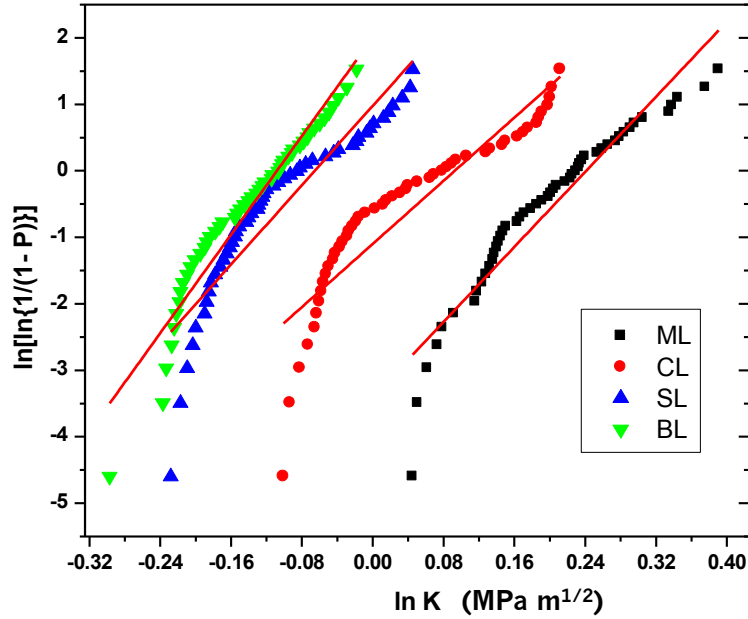


Figure 4.10: Weibull plots for the indentation toughness of all glasses.

4.5 Thermal properties of glasses

4.5.1 Differential thermal Analysis

Non-isothermal method is widely used to obtain various characteristic parameters from DTA [35-36]. In this method, the glass sample is heated up at a fixed heating rate. The characteristic transition temperatures of glass seals obtained from differential thermal analysis (DTA) at different heating rates are listed in table 4.6. T_g is the glass transition temperature, T_x is the crystallization onset temperature, T_c is the peak crystallization temperature, T_m is melting temperature of glass and T_f is the inflection point temperature. Typical DTA for ML and CL glass has been shown in fig. 4.11 (a). For obtaining T_f , DTA curves were differentiated and hence derivative differential thermal analysis (DDTA) was obtained. Then the inflection point at the peak temperature on the DDTA curve was obtained as shown in fig. 4.11(b). When the sample is heated at different heating rates, the observed crystallization peak also shifts. As shown in table 4.6, it has been observed that almost all the characteristic shift towards higher temperature with increasing heating rates, which is because of delayed nucleation in glass.

Table 4.6: Characteristic temperatures of glasses obtained from DTA.

Glass	Heating Rate β	T_g (°C)	T_x (°C)	T_c (°C)	T_m (°C)	T_f (°C)
ML	10	700	732	832	937	818
	20	728	746	843	949	824
	30	732	752	859	958	831
	40	746	758	866	967	839
CL	10	714	749	846	902	827
	20	722	753	858	913	832
	30	738	757	862	922	836
	40	752	761	869	944	842
SL	10	722	752	858	934	832
	20	736	759	867	941	839
	30	747	764	873	953	853
	40	762	770	882	960	864
BL	10	682	734	775	901	752
	20	718	741	782	927	773
	30	722	747	793	933	780
	40	731	759	813	941	802

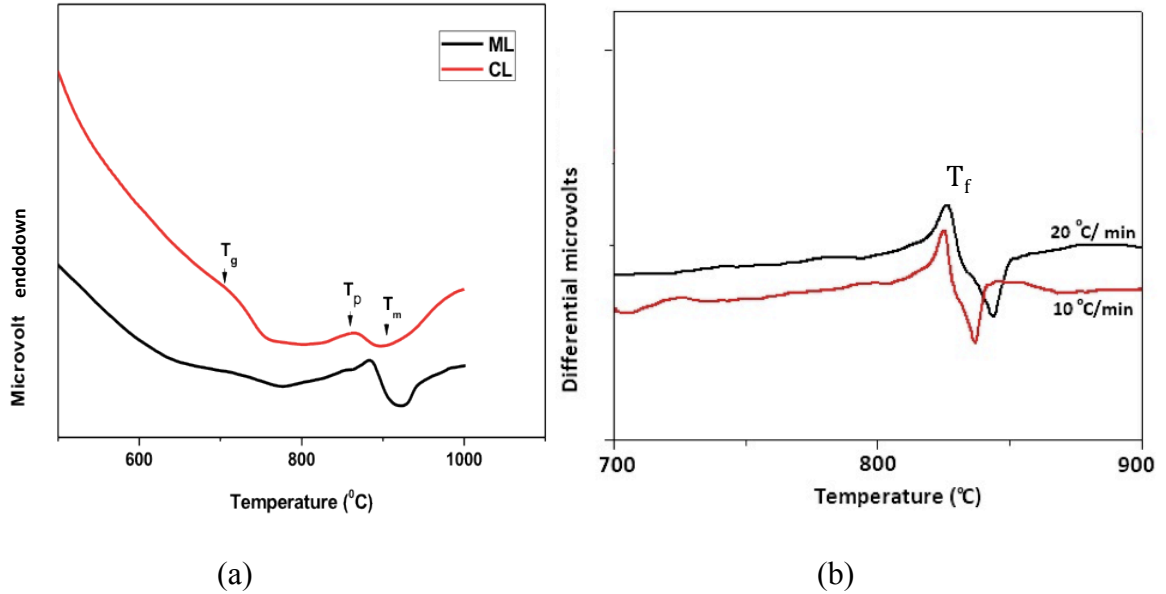


Figure 4.11:(a) Typical DTA thermograms for ML and CL glass (10 °C /min) and (b) Typical DDTA curve for ML glass sample.

In addition to this, stability of glass sealant cannot be determined only by parameters like T_g and T_c as neither of them can be determined accurately. T_g is a kinetic parameter and the underlying thermodynamic basis for glass formation is $T_g \rightarrow T_c$ as variation in temperature with time $(\frac{dT}{dt}) \rightarrow 0$. The properties of glasses are time dependent in glass transition region. When the time

scale required for structural rearrangement of glasses becomes comparable to the experimental time scale, then their structural relaxation occurs. During the process of structural relaxation of glasses, the configuration of glasses tries to attain equilibrium. But at sufficiently low temperatures, the time scale becomes so long that any rapid change in temperature can “freeze-in” the liquid structure [37]. T_g and T_c values are comparatively low for BL glasses, which can be attributed to increase in number of non-bridging oxygens as well as larger size difference between La^{3+} (1.03Å) and Ba^{2+} (1.35Å) within the glass matrix [38-39].

4.5.2 Coefficient of thermal expansion

The temperatures obtained from dilatometer (5 °C/min) have been listed in table 4.7. The T_g is lowest for BL glass, which is due to higher NBO's in this glass. Additionally, BL glass is also having highest density (table 4.1), which is due to its higher atomic weight. The higher density value of BL glass also indicates larger cross-linking as well as higher non-bridging oxygen within the glass structure [39].

Table 4.7: Characteristic temperatures of glasses obtained from dilatometry.

Glass	$T_g(^{\circ}C)$ (DIL)	$T_s(^{\circ}C)$ (DIL)
ML	698	726
CL	710	740
SL	718	748
BL	678	701

Fig. 4.12 shows the variation of CTE values obtained from dilatometer as a function of heat-treatment duration for all glasses (at 850 °C). The measurements of CTE were carried out between room temperature upto temperature which is slightly above the glass softening temperature. The expansion of glass is also related to the non-harmonic vibration of particles. Particularly for oxide glasses, they are determined by taking into consideration the attraction between ions [40] as follows:

$$F = 2Z/d^2 \quad (4.18)$$

Where F is force of attraction, Z is equivalent of positive ions and d is the distance between positive and negative ions. If the interatomic potential well of an atom is parabolic, then the atomic displacement and driving force are linearly proportional to each other. In that case, the atoms undergo harmonic oscillation, without change in their position yielding no thermal

expansion during heating process. Generally, potential well is not parabolic as Lennard-Jones potential show more resistance to compression than tension. Hence, thermal vibrations tend to drive atoms apart causing thermal expansion. As the time duration of heat-treatment increases, the amplitude of thermal vibrations within the glass network also gets enhanced. The general increase in volume with temperature is mainly attributed to increased amplitude of atomic vibrations about a mean position [41] i. e.

$$E = - (e^2/4\pi\epsilon_0 R) + (B/R^n) \quad (4.19)$$

where e is the charge of ion, B is constant and R is the interatomic distance between ions. The first term is due to attraction between ions and second term indicates repulsion. Repulsive term changes more rapidly as compared to attractive term, with atomic separation. Moreover, in asymmetric potential well, the atoms spend more time at $r > r_0$, where r_0 is the equilibrium distance at absolute zero. This may subsequently decrease the attraction between ions and increase the bond length leading to lattice expansion of glass network. Figure 4.12 clearly depicts the variation of CTE in accordance of $CTE_{BL} > CTE_{SL} > CTE_{CL} > CTE_{ML}$. This can be associated with high ionic radius of Ba^{2+} ($1.35\text{\AA}$) among all the alkaline earth metals under present investigation [32]. The CTE value of ML glass ceramic is quite low as compared to the value of CTE for Crofer 22APU metallic interconnect ($11.8 \times 10^{-6} / ^\circ\text{C}$) and YSZ ($10.5 \times 10^{-6} / ^\circ\text{C}$). As the time duration of heat-treatment increases from 5 h to 750 h, the CTE of CL and BL sample gets raised sharply than ML and SL sample. Both SL and BL glass compositions display required range of CTEs for SOFC applications. The CTE of investigated glass ceramics (GC) vary in range $[9.1-10.8 \times 10^{-6} / ^\circ\text{C}]$, which is in good agreement with CTE of Crofer 22APU and YSZ. It is well reported in the literature that the difference of $[1-1.5 \times 10^{-6} / ^\circ\text{C}]$ among various components of SOFC is acceptable [42]. CTE is attributed to the asymmetric potential well in the systems [43]. Materials with strong bonds show small change in thermal expansion coefficient. For good sealing, the CTE should remain constant with the devitrification of material in order to attain stability over longer periods of time.

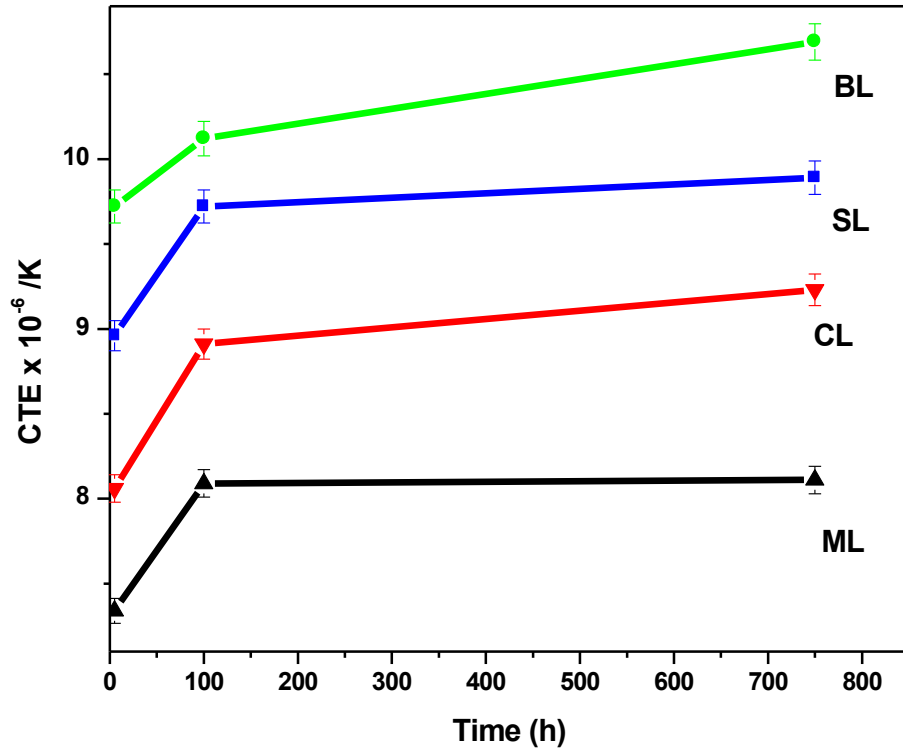


Figure 4.12: Variation of CTE with heat-treatment duration for glasses heat-treated at 850 °C.

For SL glass, the CTE remains relatively constant and displays acceptable range as the material devitrifies. It shows that the SL glass may work as ideal sealing material in oxidizing atmosphere. CTE mismatch between the glass and components of SOFC lead to thermal stress, which is given by the following relation [44-45]:

$$\sigma = CE \int (\alpha_g - \alpha_m) dT \quad (4.20)$$

where E is Young's modulus, C is Geometrical constant, α_g and α_m are CTE of glass and material. Thermo-mechanical stresses arise from differences in the material properties and temperature gradient. CTE mismatch between the seal glass and in adjoining components can cause tensile thermal stress ($CTE_{comp} > CTE_{glass}$) or compressive thermal stress ($CTE_{glass} > CTE_{comp}$) at interface [46]. Cracks and pores may form at interface due to tensile stress and delamination of glass seal occurs due to compressive / shear stress. CTE increases due to asymmetric structure of borate structural groups that decreases network connectivity [47].

4.5.3 Crystallization kinetics

Glass ceramics in general exhibit some crystalline phases produced by controlled crystallization of glasses [48]. The phenomena of controlled crystallization involves two stage heat-treatment i.e. nucleation and crystallization. In the nucleation stage, small nuclei are formed within the parent glass and after the formation of stable nuclei, crystallization proceeds by growth of new crystalline phase. Nucleation and crystallization are very important parameters during glass preparation that should be completely understood to obtain desired microstructure and properties. For that purpose, various thermodynamic parameters like Lasocka parameter, activation energy of crystallization, frequency factor and Avrami parameter have been evaluated. Along with these parameters, crystallization constants as a function of different temperatures as well as different heating rates have also been studied.

T_g and its dependence on heating rates can be given by the following original empirical Lasocka equation [49]:

$$T_g = A + B \ln \beta \quad (4.21)$$

Here A is the glass transition temperature when the heating rate is 1°C min^{-1} . B depends upon the composition of glass and gives the time response of various configurational changes occurring during the glass transition region. The parameter B depends on the chemical nature of modifier. A graph is plotted between $\ln [\beta]$ and $1000/T_g$ which gives straight line and the data obtained were well fitted in straight lines.

Table 4.8: Constants A and B, frequency, Avrami parameter and activation energy for all the glasses.

Glass	A ($^\circ\text{C}$)	B	Frequency (s^{-1})	Avrami Parameter (n)	Activation energy(kJ/mol)
ML	629.05	31.46	3.19×10^8	1.43	382
CL	647.65	26.72	1.54×10^{11}	1.68	273
SL	656.45	27.53	9.51×10^{11}	1.84	291
BL	606.09	34.59	7.53×10^{10}	1.72	308

The slope and intercept gives parameter B and A, respectively which are listed in table 4.8. The activation energy of glass crystallization (E_c) has been calculated using Augis and Benett model [35]. Activation energy is the threshold energy above which any transformation can take place in the activated complex. Generally, total activation energy is composed of two parts [50]:

$$E_c = aE_N + bE_G \quad (4.22)$$

E_N is the activation energy of nucleation and E_G is the activation energy of growth. a and b are parameters related to Avrami parameter and $a + b = 1$. During the beginning process, nucleation dominates i.e. $b = 0$. By the end of crystallization process, $a = 0$ because only the growth process is going to dominate. The activation energy at the peak of crystallization is obtained using following relation [35]:

$$\ln (T_c/\beta) = E_c/RT_c + \ln v \quad (4.23)$$

v is defined as the number of attempts, which are made by the nuclei/second for overcoming the energy barrier, and β is the heating rate. v provides information regarding the available nucleation sites for crystal growth. The values of frequency and activation energy are listed in table 4.8. The values of frequency are obtained from the intercept of equation 4.23 by the least squares fitting method [35,51]. Maximum value of v will indicate instability of glass. ML glass has lowest v followed by BL glass, hence exhibiting lowest nucleation sites. Lowest v value and highest E_c for ML implies smaller crystallization tendency in these glasses, which is in good agreement with X-ray diffraction pattern (discussed later). Even after 100 h treatment, the coupled BL and CL glasses did not exhibit crystallization. Due to lower activation energy and higher v value in case of CL and SL glasses, crystallization could not be avoided after 100 h treatment, as is clear from the XRD pattern (discussed later). Experimentally, the activation energy of crystallization can be explained on the basis of field strength of alkaline earth metals present in glasses. The field strengths of Mg^{+2} , Ca^{2+} , Sr^{2+} and Ba^{2+} are 0.45, 0.33, 0.30 and 0.24, respectively [43]. Higher the field strength, higher should be the activation energy. Hence ML glass can be expected to have highest activation energy of crystallization and is in agreement also (table 4.8). But for other three glasses, $E_{BL} > E_{SL} > E_{CL}$ trend has been followed. However, in the present case reverse trend is observed for the activation energy of crystallization. Basically, seal glasses are multicomponent oxides. Network modifiers have low field strength (< 0.35) and higher coordination number than glass former [41]. The network modifier disrupts glass network structure, occupy random positions in between polyhedral and maintain local charge neutrality [52]. The properties of glass seal depend upon the cation oxygen bond-length and bond angles, coordination number of cations, degree of network connectivity and local ordering in network structure [53-54]. Apart from field strength, the electronegativity and local arrangement of atoms also play very important role in crystallization of glasses. The

electronegativity of La^{3+} , Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} is 1.08, 1.31, 1.04, 0.99 and 0.97, respectively. The difference in electronegativity (DE) of La^{3+} and modifier cations follows the order $\text{DE}_{\text{ML}} > \text{DE}_{\text{BL}} > \text{DE}_{\text{SL}} > \text{DE}_{\text{CL}}$. This is in complete agreement with the trend obtained for E_c . The lowest electronegativity difference between glass modifying La^{3+} and Ca^{2+} cations may lead to lowest activation energy of crystallization in CL glass as compared to other three glasses. Hence, in the present study, electronegativity plays a crucial role instead of field strength in determining the trend followed by activation energy. In addition to this, the activation energy may also be related to the first formed crystalline phases in glass matrix [55]. Avrami parameter, which is related to morphology of crystal growth, has been found to be non-integer for all the glasses. It can be calculated by using following equation [36]:

$$[\text{dln}(\Delta y)/\text{d}(\Delta y)] = -nE_c/R \quad (4.24)$$

where Δy is vertical displacement at temperature T of DTA exotherm. The value of n is calculated using Piloyan plot between $\ln(\Delta y)$ and $1000/T$ as shown in fig.4.13.

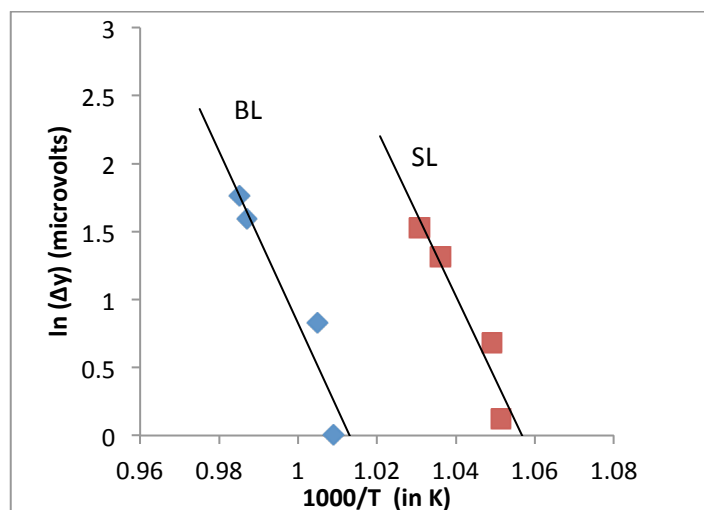


Figure 4.13: Piloyan's plot for BL and SL glass.

The values of n are given in table 4.8. A non-integer value of n indicates the possible occurrence of two crystallization mechanisms simultaneously working during amorphous-crystalline transformation [55]. It might be possible that ASiO_3 ($A = \text{Sr}, \text{Ba}$) crystalline phase grow one-dimensionally in the early stage of crystallization in these glasses. More details are discussed in next section. Apart from this, the rate of crystallization k has been evaluated using following relations [51,56]:

$$k_y(T) = v \exp(-(E/RT)(T_x - T_g)/T_m) \quad (4.25)$$

$$\text{and} \quad k_b(T) = v \exp(-(E/RT)H_r) \quad (4.26)$$

T_x is the crystallization onset temperature, T_m is melting temperature of glass and Hruby parameter $H_r = (T_x - T_g)/(T_m - T_c)$. Minimum values of k indicate decrease in crystallization and hence increase in glass forming ability. The new k criterion takes $(T_c - T_f)$ into account, where T_f is the inflection point temperature [51]. It remains almost stable and hence temperature as well as rate independent i.e.

$$k_f(T) = v \exp(-(E/RT)(T_c - T_f)/T_f) \quad (4.27)$$

It is quite observable from table 4.9 that $k_y(T)$ and $k_f(T)$ are quite independent of heating rates, whereas $k_b(T)$ shows inconsistent variation. This may be due to the fact that thermodynamic factors like $(T_c - T_f)/T_f$ and $(T_x - T_g)/T_m$ are involved in the evaluation of $k_y(T)$ and $k_f(T)$ and parameter H_r is also used to determine $k_b(T)$. Hence, $k_b(T)$ cannot be regarded as a stability criteria in the present glasses. CL and SL glasses possess higher crystallization constants in comparison to ML and BL glass which is in accordance with their frequency factors (v). Hence these parameters play a substantial role in determining the nature of glasses.

Table 4.9: Crystallization constants for all the glasses.

	β	$k_y(T)$			$k_b(T)$			$k_f(T)$		
		$k_y(T_g)$	$k_y(T_c)$	$k_y(T_f)$	$k_b(T_g)$	$k_b(T_c)$	$k_b(T_f)$	$k_f(T_g)$	$k_f(T_c)$	$k_f(T_f)$
ML	10	3.186×10^8	3.187×10^8	3.189×10^8	3.144×10^8	3.150×10^8	3.149×10^8	3.188×10^8	3.188×10^8	3.188×10^8
	20	3.187×10^8	3.188×10^8	3.189×10^8	3.165×10^8	3.168×10^8	3.167×10^8	3.187×10^8	3.188×10^8	3.188×10^8
	30	3.187×10^8	3.188×10^8	3.189×10^8	3.161×10^8	3.164×10^8	3.164×10^8	3.186×10^8	3.187×10^8	3.187×10^8
	40	3.188×10^8	3.189×10^8	3.190×10^8	3.173×10^8	3.175×10^8	3.174×10^8	3.186×10^8	3.187×10^8	3.187×10^8
CL	10	1.538×10^{11}	1.539×10^{11}	1.539×10^{11}	1.508×10^{11}	1.511×10^{11}	1.511×10^{11}	1.539×10^{11}	1.539×10^{11}	1.539×10^{11}
	20	1.539×10^{11}	1.539×10^{11}	1.539×10^{11}	1.511×10^{11}	1.515×10^{11}	1.514×10^{11}	1.539×10^{11}	1.539×10^{11}	1.539×10^{11}
	30	1.539×10^{11}	1.539×10^{11}	1.539×10^{11}	1.524×10^{11}	1.526×10^{11}	1.526×10^{11}	1.539×10^{11}	1.539×10^{11}	1.539×10^{11}
	40	1.54×10^{11}	1.54×10^{11}	1.54×10^{11}	1.534×10^{11}	1.535×10^{11}	1.534×10^{11}	1.539×10^{11}	1.539×10^{11}	1.539×10^{11}
SL	10	9.501×10^{11}	9.502×10^{11}	9.502×10^{11}	9.375×10^{11}	9.390×10^{11}	9.388×10^{11}	9.502×10^{11}	9.503×10^{11}	9.503×10^{11}
	20	9.504×10^{11}	9.504×10^{11}	9.504×10^{11}	9.404×10^{11}	9.417×10^{11}	9.414×10^{11}	9.501×10^{11}	9.502×10^{11}	9.502×10^{11}
	30	9.505×10^{11}	9.509×10^{11}	9.506×10^{11}	9.439×10^{11}	9.446×10^{11}	9.445×10^{11}	9.505×10^{11}	9.505×10^{11}	9.505×10^{11}
	40	9.508×10^{11}	9.508×10^{11}	9.508×10^{11}	9.476×10^{11}	9.479×10^{11}	9.479×10^{11}	9.505×10^{11}	9.505×10^{11}	9.505×10^{11}
BL	10	7.517×10^{10}	7.518×10^{10}	7.518×10^{10}	7.412×10^{10}	7.422×10^{10}	7.420×10^{10}	7.524×10^{10}	7.524×10^{10}	7.524×10^{10}
	20	7.524×10^{10}	7.525×10^{10}	7.525×10^{10}	7.486×10^{10}	7.488×10^{10}	7.488×10^{10}	7.528×10^{10}	7.528×10^{10}	7.528×10^{10}
	30	7.524×10^{10}	7.525×10^{10}	7.525×10^{10}	7.480×10^{10}	7.484×10^{10}	7.483×10^{10}	7.527×10^{10}	7.527×10^{10}	7.527×10^{10}
	40	7.524×10^{10}	7.524×10^{10}	7.524×10^{10}	7.472×10^{10}	7.477×10^{10}	7.476×10^{10}	7.527×10^{10}	7.527×10^{10}	7.527×10^{10}

4.5.4 Fluctuation free volume and bulk thermal expansion coefficient

According to the concept of fluctuation free volume, the transition of an amorphous substance from a liquid to solid state is accompanied with decrease in fraction of fluctuation free volume, f_g [57]

$$f_g = (V_f/V) \quad (4.28)$$

V_f is the fluctuation free volume and is the sum of the volumes, V_h of N fluctuation holes ($V_f = V_h N$) which are formed due to local excitation caused by deviation of interatomic distance between adjacent kinetic units from mean distance r_0 [58]. V is the volume of glass at T_g . The relation between fraction of fluctuation free volume (f_g) and activation energy as follows:

$$E_g/RT_g = 1/f_g \quad (4.29)$$

According to Frenkel equation [59], the abrupt change in coefficient of thermal expansion α_f which is associated with increase in number of microvoids (free volume) upon heating of glass can be determined merely by the fraction f_g :

$$\alpha_f T_g = f_g \ln(1/f_g) \quad (4.30)$$

The values of f_g and α_f at various heating rates are listed in table 4.10.

Table 4.10: Fluctuation free volume (f_g) and bulk thermal expansion coefficient (α_f) for all the glasses.

Glass	Heating Rate β ($^{\circ}\text{C}/\text{min}$)	f_g	α_f
ML	10	2.12×10^{-2}	8.39×10^{-5}
	20	2.18×10^{-2}	8.33×10^{-5}
	30	2.19×10^{-2}	8.32×10^{-5}
	40	2.21×10^{-2}	8.29×10^{-5}
CL	10	3.01×10^{-2}	1.07×10^{-4}
	20	3.03×10^{-2}	1.06×10^{-4}
	30	3.08×10^{-2}	1.06×10^{-4}
	40	3.12×10^{-2}	1.06×10^{-4}
SL	10	2.84×10^{-2}	9.87×10^{-5}
	20	2.88×10^{-2}	9.77×10^{-5}
	30	2.91×10^{-2}	9.76×10^{-5}
	40	2.95×10^{-2}	9.75×10^{-5}
BL	10	2.57×10^{-2}	1.01×10^{-4}
	20	2.68×10^{-2}	1.01×10^{-4}
	30	2.69×10^{-2}	1.01×10^{-4}
	40	2.71×10^{-2}	1.01×10^{-4}

With increasing heating rate, f_g is increasing which indicates that the number of bonds within this glass must have decreased. This ultimately leads to increase in free volume for the rearrangement of kinetic units in the glass matrix. Consequently, degree of connectivity of the glass-forming network decreases. In the present case, CL glass exhibits highest fluctuation free volume. This is in agreement with the low activation energy of crystallization required for this glass. f_g also follows the trend $f_g(\text{CL}) > f_g(\text{SL}) > f_g(\text{BL}) > f_g(\text{ML})$. This signifies that a glass with higher activation energy possesses lower free volume which goes in accordance with eq. (4.29). At the same time, ML and SL glasses have exhibited small jump in α_f in comparison to CL and BL glasses. In the present case, CL and BL glasses also exhibited highest change in linear CTE (section 4.5.2). BL glass has exhibited highest jump in α_f . Literature also reports that same behavior is also exhibited by barium containing glasses [14, 32, 39]. In addition to this, higher covalency of glass network leads to low abrupt change in α_f [43]. Materials with strong bonds show small change in coefficient of thermal expansion. This implies that ML glass network exhibits strong bonds. BL glass network have highest NBO's and hence loose network, which may be responsible for its high α_f .

4.6 Interaction of glasses with Crofer 22APU interconnect

4.6.1 X-ray diffraction of coupled glasses

The pristine glasses were found to be amorphous in nature exhibiting broad halo in the diffractogram as shown in fig. 4.1

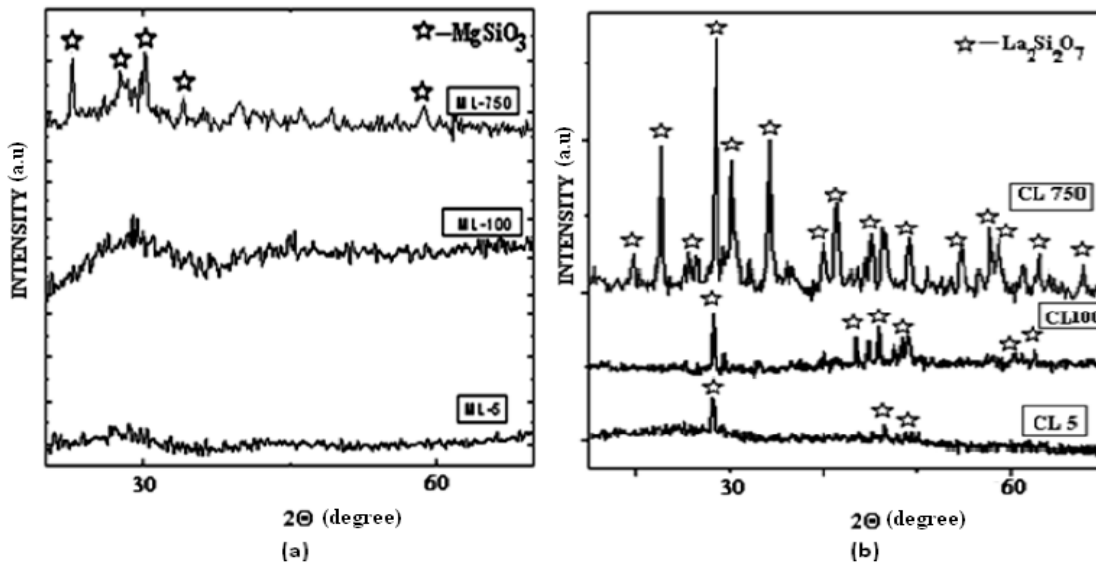
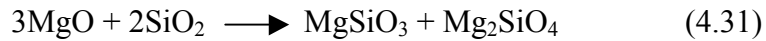
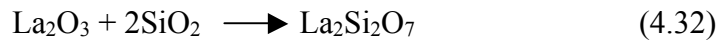


Figure 4.14: X-ray diffractogram for coupled (a) ML glass and (b) CL glass (heat-treated at 850 °C for 5, 100 and 750 h).

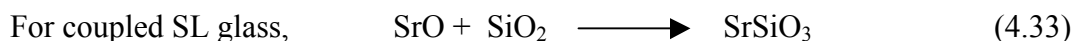
Fig. 4.14 (a-b) and 4.15 (a-b) show the XRD spectrum of the ML, CL, SL and BL glass seals coupled between the Crofer 22APU plates, which were subjected to heat-treatment for 5, 100 and 750h (at 850 °C). After 5h heat-treatment, all coupled glasses except CL glass have broad halo in diffractogram, which depicts their amorphous nature. For coupled ML glass, no phase formation was observed after 100 h treatment, but MgSiO_3 phase precipitated out during 750 h treatment (fig. 4.14(a)). Zdaniewski [60] reported that for MgO-SiO_2 based glass systems, the growth of a crystalline phase is initiated by the formation of silica rich solid solution. Subsequently, the substitution of Mg^{2+} occurs at different sites of unit cell leading to the formation of Mg_2SiO_4 and MgSiO_3 phase. The phase formation follows the following mechanism:



In case of coupled CL glass (fig. 4.14 (b)), ordered $\text{La}_2\text{Si}_2\text{O}_7$ pyrochlore phase was formed during 5 h treatment. However, its volume fraction increased upon prolonged period of heat-treatment. Additionally, the XRD analysis revealed that an almost complete crystallization could be achieved after 750 h treatment of coupled CL glass. The change in peak intensity with heat-treatment duration for coupled CL glass is high suggesting fast crystallization. The mechanism of phase formation could be given as:



The high degree of crystallization of coupled CL glass could be due to high nucleation rate and its lowest activation energy of crystallization. A high degree of crystallization is sometimes required to enhance the thermo-mechanical properties like CTE and viscosity of the sealant, which enhances their bulk stability, provided the formed crystalline phases should not be detrimental [61-62]. Along with this, microstructural modification should also be prevented during the operation of SOFC at high temperature (800-1000 °C). Prolonged heat-treatment of SL glass shows the formation of SrSiO_3 [ICDD-080057] phase subsequently followed by Sr_2SiO_4 [ICDD-181281] phase as shown in fig. 4.15 (a). For coupled BL glass (4.15 (b)), no phase formation was observed even after 100 h heat-treatment at 850 °C. After prolonged heat-treatment (750 h), BaSiO_3 [ICDD-702112] phase precipitated along with sanbomite BaSi_2O_5 [ICDD-250073] phase. Following reaction kinetics can be proposed to understand the formation of different crystalline phases in coupled seal:



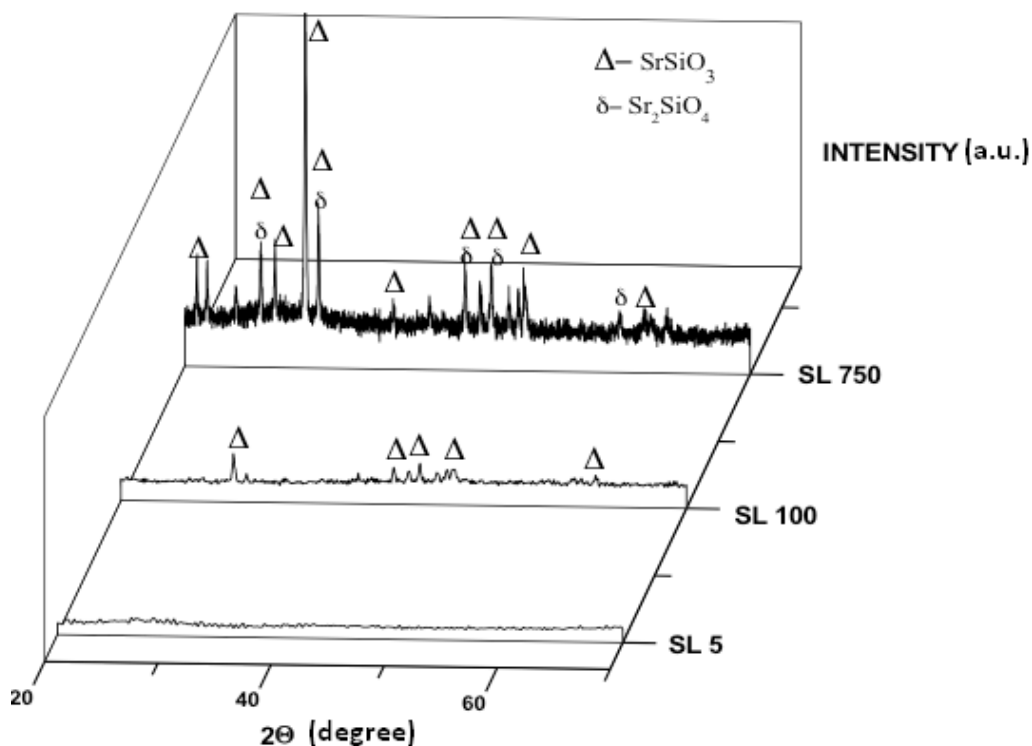
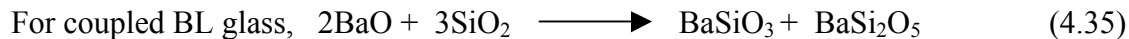


Figure 4.15(a): X-ray diffractogram for coupled SL glass.

Similar results have been reported by other researchers in different glass compositions [55, 63]. Initially ASiO_3 ($A=\text{Mg, Ca, Sr, Ba}$) phase is formed and at later stage of heat-treatment, these phases get converted to more thermodynamically stable phases such as A_2SiO_4 . The volume fraction of SrSiO_3 increased and hence high degree of crystallization was observed with increasing heat-treatment duration. Crystallization could not take place after 100 h heat-treatment in both ML and BL glasses. In addition to this, lower crystallization after prolonged heat-treatment is observed for these two glasses. In other words, coupled BL and ML glasses show controlled crystallization as shown in fig. 4.14 (a) and 4.15(b). The XRD pattern of coupled glasses could not form any crystalline phases having iron and chromium as constituents. However, the possibility of chromium and iron diffusion from crofer to glasses could not be ruled out. However, their migration percentage might be less than the detection

limit of our XRD (2%) unit though colour of glass seal has changed from white to slightly bluish. Along with this, Cr_2O_3 and $(\text{Mn}, \text{Cr})_3\text{O}_4$ could not be observed as is evident from figs. 4.14 and 4.15. $(\text{Mn}, \text{Cr})_3\text{O}_4$ spinel layer formed at the Crofer 22APU interface is assumed to be the active barrier layer for the diffusion of both glass and the Crofer 22APU elements.

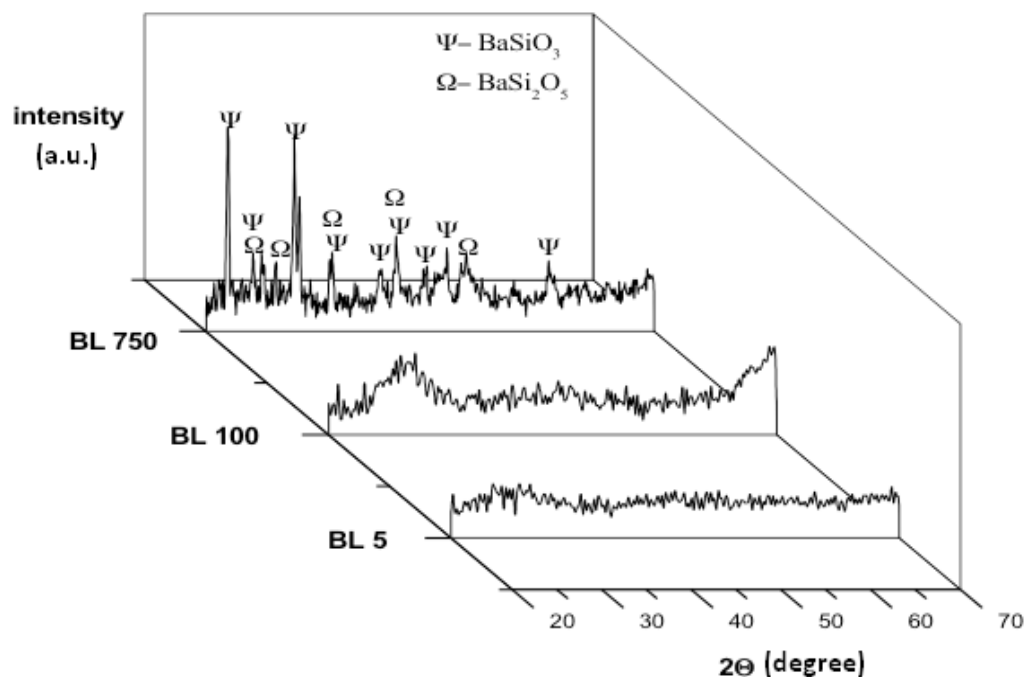


Figure 4.15(b): X-ray diffractogram for coupled SL glass.

It is noteworthy that the remaining glassy phase in GC acts as major factor for deciding the flow behavior of the GC seal and plays a crucial role in determining the reaction kinetics during chemical interaction between glass seal and SOFC components. Also, such a high amount of glassy phase present in the GC's is expected to exhibit self-healing behavior during SOFC operation [63]. The stresses and the lower flowability of the devitrified phases can create pores and cracks in the glass as well as at the interface [64]. Higher temperature and longer time is required for a glass to devitrify means high devitrification resistance of that glass. Devitrification arises due to very small nuclei formed during glass making, heterogeneity in glass network structure, surface flaws and residual stress from mechanical polishing [41, 52, 54, 65]. Formers can degrade the devitrification resistance of glass [66]. Firstly, the degree of network connectivity decreases with increased fraction of NBO containing structural units. Secondly, different type of structural units induces heterogeneity in glass structure. La_2O_3

containing glasses generally tend to form isolated, small, energetically favourable, and phase ordered clusters. These generally contain La-O-La clusters which act as nucleation sites for devitrification of glass [67-68]. The extent of devitrification increases with thermal treatment time until a stable state is reached.

4.6.2 Sealing and microstructural analysis

During scanning electron microscopy sample preparation through grinding, polishing and ultrasonic cleaning, the glasses did not detach from the glass surface. This suggests that strong bonds have been formed between glass/ Crofer 22APU. For present interconnect-seal interfacial studies, the experiments have been conducted in an oxidizing atmosphere. Air promotes chromate phase formation whereas H_2/H_2O promotes iron/chromium containing phases at interface [69]. The chemical reaction at the interface is controlled by the diffusion process, since diffusion must occur prior to the chemical reaction. Diffusion of Crofer 22APU elements into glass breaks the glass network structure and enhances the devitrification of glass [65]. At 800 °C, chromium comes from Crofer 22APU alloy and reacts with NBOs to form Cr_2O_3 . During the later stage of this process, Cr_2O_3 can condense and form Cr_2O_3 film at the interface [70]. Sometimes the chromia layer reacts with seal glass and causes the formation of undesirable $SrCrO_4$ and $BaCrO_4$. In the following section, diffusion couple of glasses with Crofer 22APU metallic interconnect as a function of heating durations of 5, 100 and 750 h has been investigated in order to check the interfacial stability.

4.6.2.1 ML/Crofer 22APU couple: Fig. 4.16 (a) shows the SEM micrograph of Crofer 22APU/ML couple heat-treated for 5 h at 850 °C. The interface clearly shows residual porosity within the bulk glass ceramic attributed to thermal expansion mismatch between glass and metallic interconnect. Moreover, mostly amorphous state of coupled glass after 5h treatment must be responsible for its internal brittleness. The cross section of this diffusion couple was further investigated using X-ray dot mapping in order to detect the possible diffusion of chromium from Crofer 22APU interconnect into the glass sealant. However, some diffusion of chromium could be seen into the glass ceramic as is clear from fig. 4.16 (b). The diffusion of iron from Crofer 22APU has also taken place. Additionally, interface was found to be magnesium rich, which has also diffused out of the glass. Fig. 4.17 (a) shows the SEM micrograph of Crofer 22APU/ML/Crofer 22APU couple heat-treated for 100 h at 850 °C. Examination around the joining region shows very low residual porosity. Hence, relatively

better joining was observed between glass and metallic interconnect. The absence of cracks near the interface demonstrates good chemical and physical compatibility. From the line spectra shown in fig. 4.17(b), it can be observed that the diffusion of iron and chromium into the glass ceramic has taken place. Fig. 4.18 (a) shows the SEM cross-section of Crofer 22APU/ML/Crofer 22APU couple heat-treated for 750 h at 850 °C. The SEM is focused on the central part of interface. This diffusion couple reflects a remarkable difference in the microstructural behavior during the process of crystallization. The adhesion test revealed nucleation of crystalline phase from the interface and its further growth into the amorphous glass.

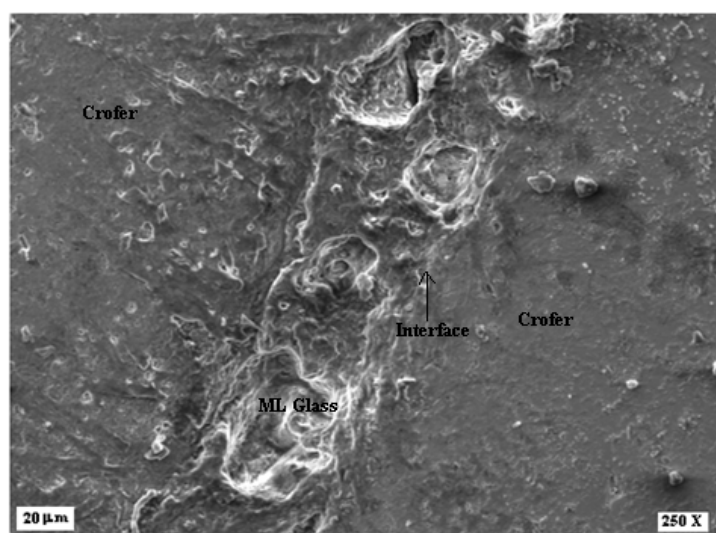


Figure 4.16 (a): Crofer 22APU/ML/Crofer 22APU diffusion couple at 850 °C for 5 h.

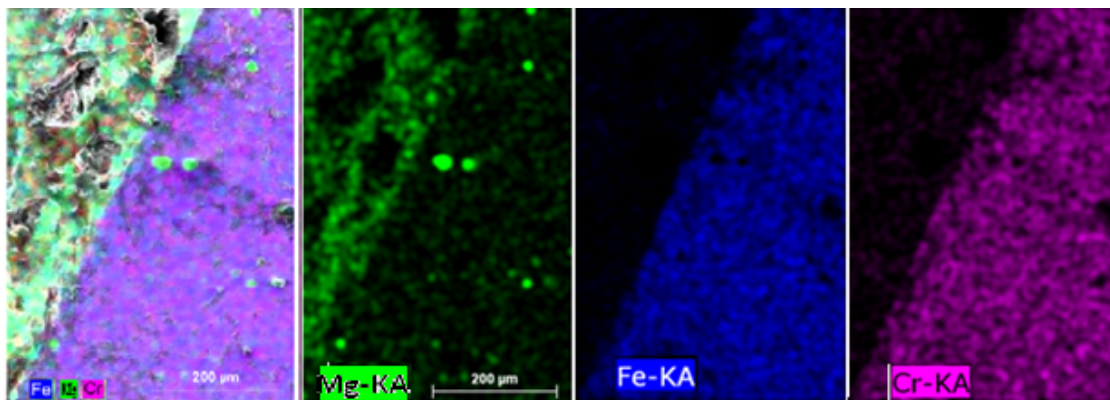


Figure 4.16 (b): X-ray dot mapping of Crofer 22APU/ML/Crofer 22APU interface.

Layers of devitrified crystalline phases were found at both interfaces. Fig. 4.18 (a) clearly depicts that MgSiO_3 phase has nucleated at the surface and then grew directionally into the dark

amorphous glass. Fig. 4.18 (c) shows the magnified image of the coupled ML glass (750 h at 850 °C) between the interface. The presence of this phase can be seen in SEM obtained for this glass. The microstructure clearly indicates that the glass is a fairly homogenous mixture of needle like crystallized phase (MgSiO_3) embedded in amorphous glassy phase.

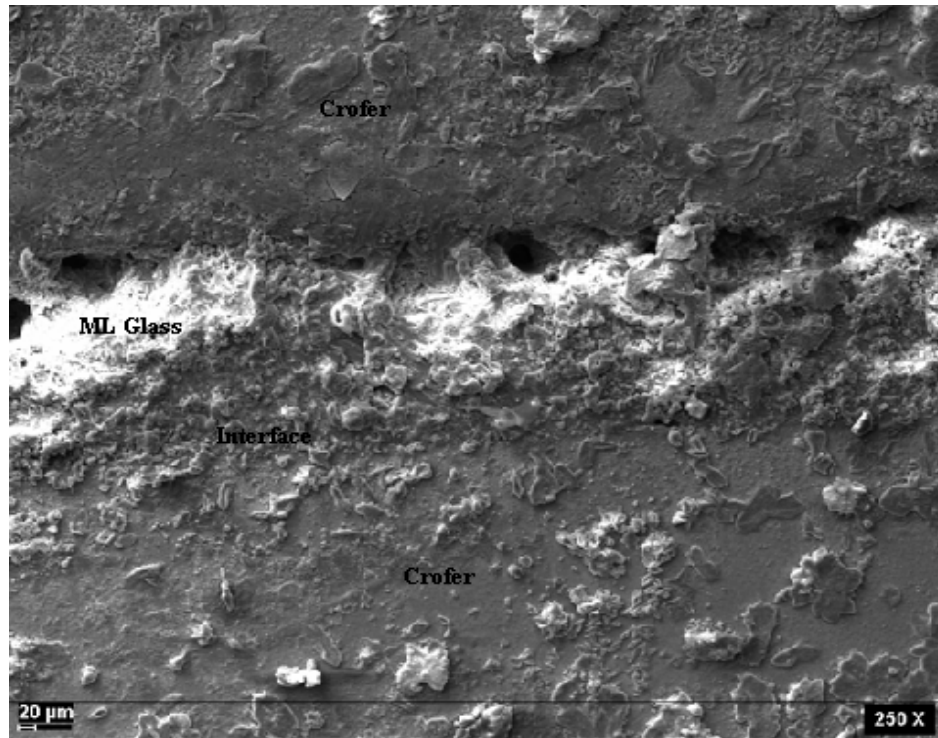


Figure 4.17 (a): Crofer 22APU/ML/Crofer 22APU diffusion couple at 850 °C for 100 h.

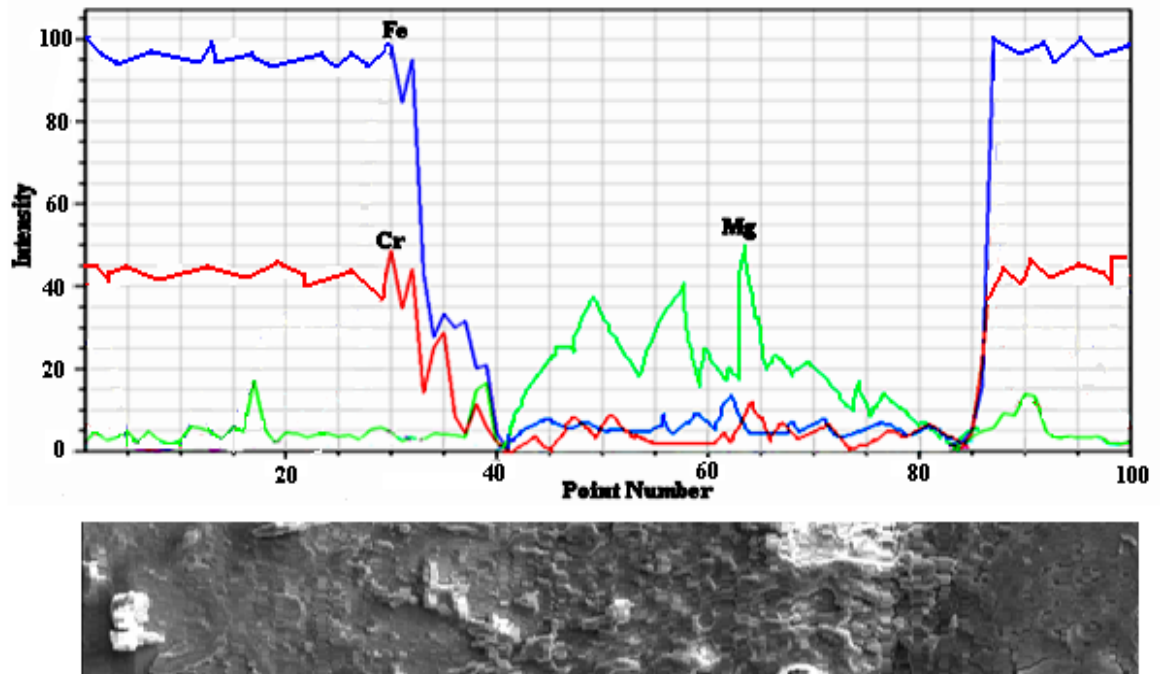


Figure 4.17 (b): EPMA of joint region shown in fig. 4.17 (a).

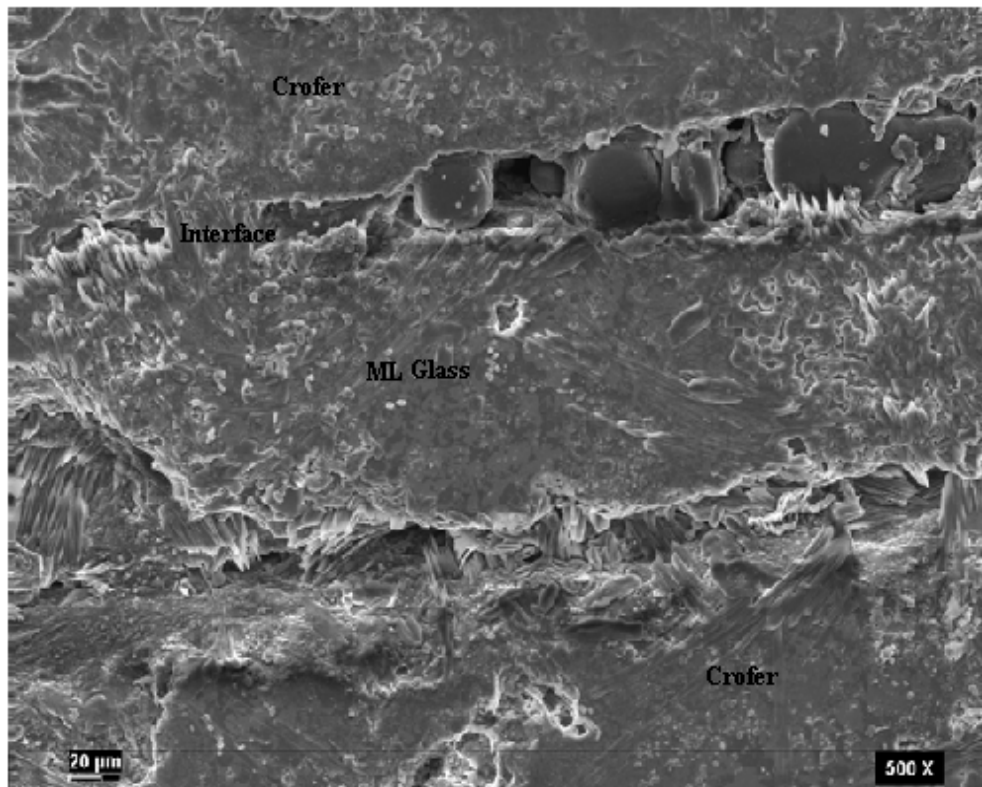


Figure 4.18 (a): Crofer 22APU/ML/Crofer 22APU diffusion couple at 850 °C for 750 h.

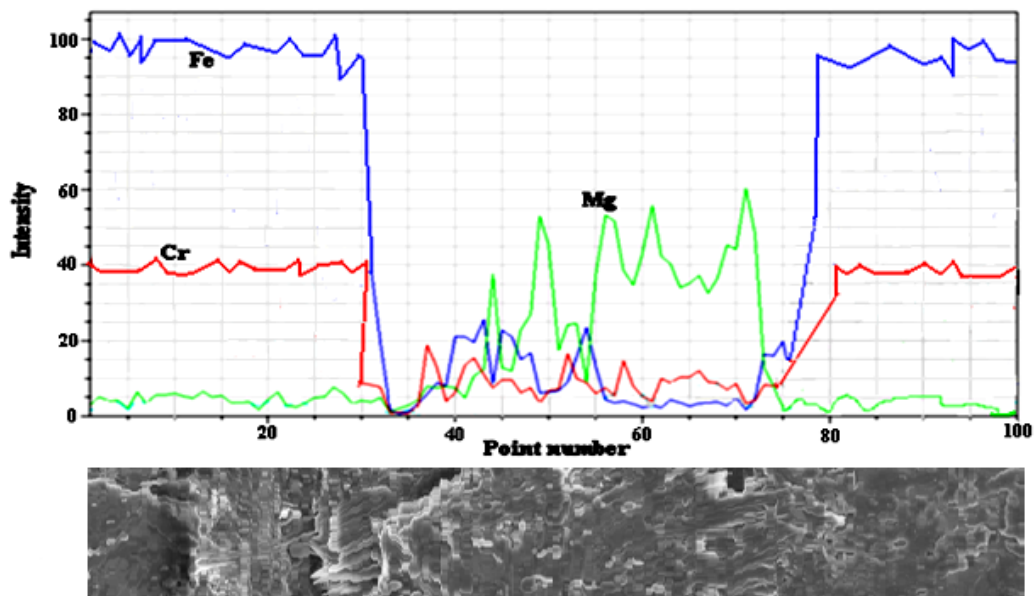


Figure 4.18 (b): EPMA line scan of joint region shown in fig.4.18(a).

This is very favourable microstructure as crystallization is controlled in the glass sealant. From the line analysis (fig.4.18 (b)), it is revealed that no new reaction products have formed between glass/ Crofer 22APU interface though the diffusion of chromium has occurred in glass seal. This further confirms the absence of any chromates, which are undesirable and detrimental for the SOFC operation [39,71].

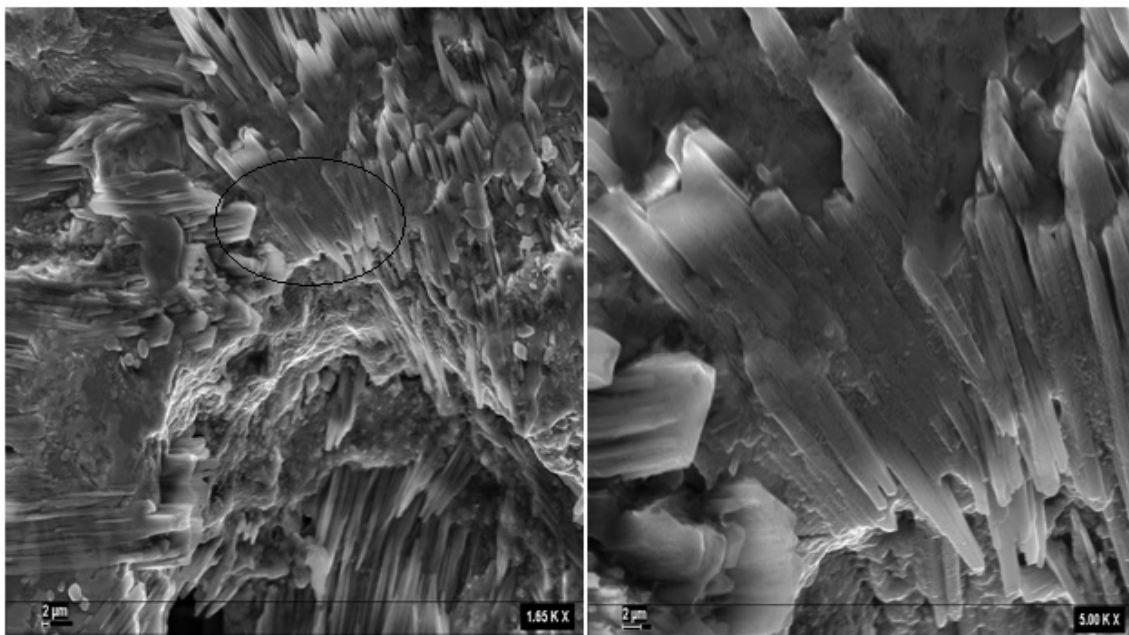


Figure 4.18 (c): Microstructure of coupled ML glass-ceramic between Crofer plates after heat-treatment of 750 h.

4.6.2.2 CL/ Crofer 22APU couple: Fig. 4.19(a) shows the interface zone of Crofer 22APU/CL/Crofer 22APU couple heat-treated for 5 h at 850 °C. Observable delamination at the glass/interconnect interface is seen which can be due to greater CTE mismatch among them. Virtually, low sealing tendency is observed at the interface. Extensive cracking at the interface was observed which also propagated within the bulk glass ceramic, though no corrosion was observed at the joint region. The glass ceramic has high porosity which could be due to the formation of some volatile species.

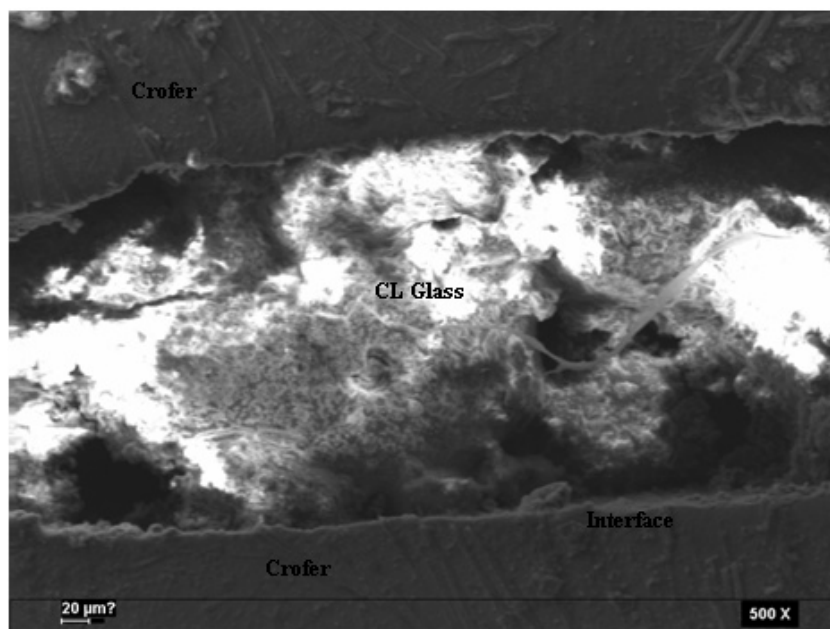


Figure 4.19 (a): Crofer 22APU/CL/Crofer 22APU diffusion couple at 850 °C for 5 h.

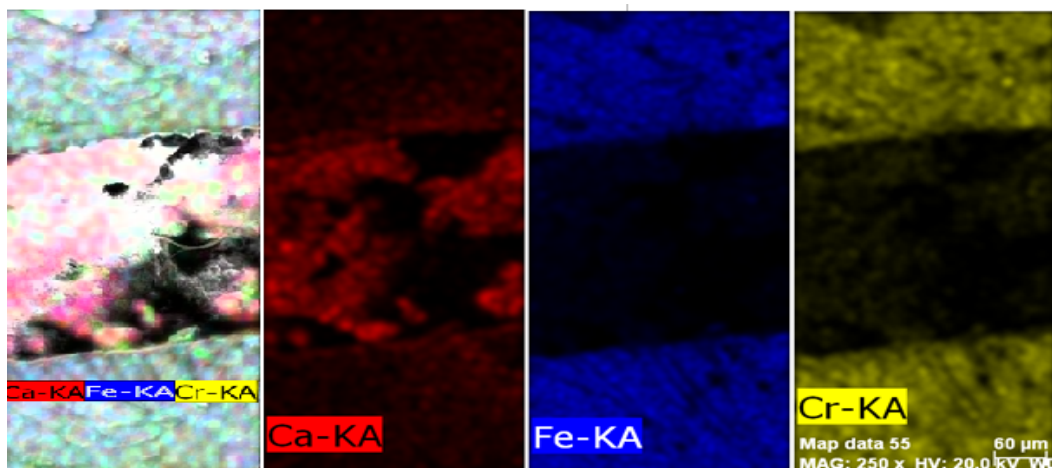


Figure 4.19 (b): X-ray dot mapping of Crofer 22APU/CL/Crofer 22APU interface.

Relatively low amount of chromium and iron diffusion could be observed in the seal as is clear from X-ray dot mapping (fig. 4.19 (b)) though appreciable amount of Ca^{2+} ions diffused out from the glass. For Crofer 22APU/CL/Crofer 22APU couple (fig. 4.20 (a)) heat-treated at 850 °C for 100 h, the absence of cracks near the interface demonstrates good adhesion of glass to metallic interconnect.

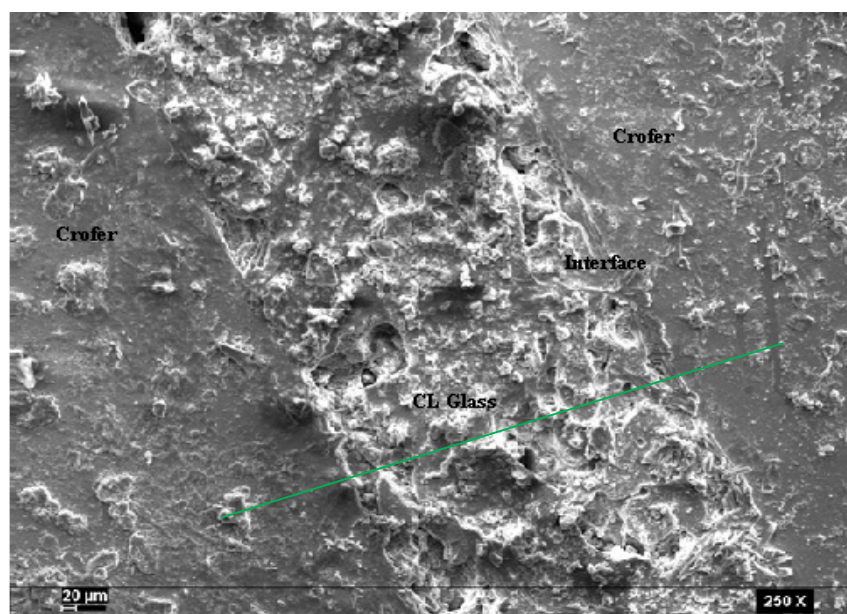


Figure 4.20 (a): Crofer 22APU/CL/Crofer 22APU diffusion couple at 850 °C for 100 h.

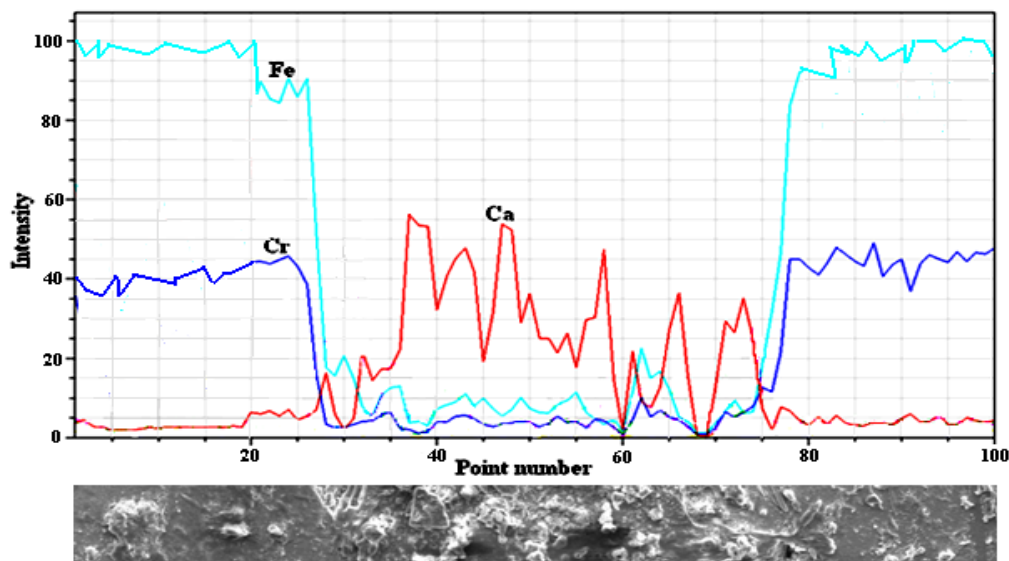


Figure 4.20 (b): EPMA line scan of joint region shown in fig. 4.20 (a).

The bulk glass microstructure and interface are more or less defect free. No gaps could be observed at the edges of the joints and the glass ceramic is bonded well to the interconnect. Iron and chromium has diffused to some extent as is clear from fig. 4.20(b). Diffusion of calcium is also seen on either side of interface.

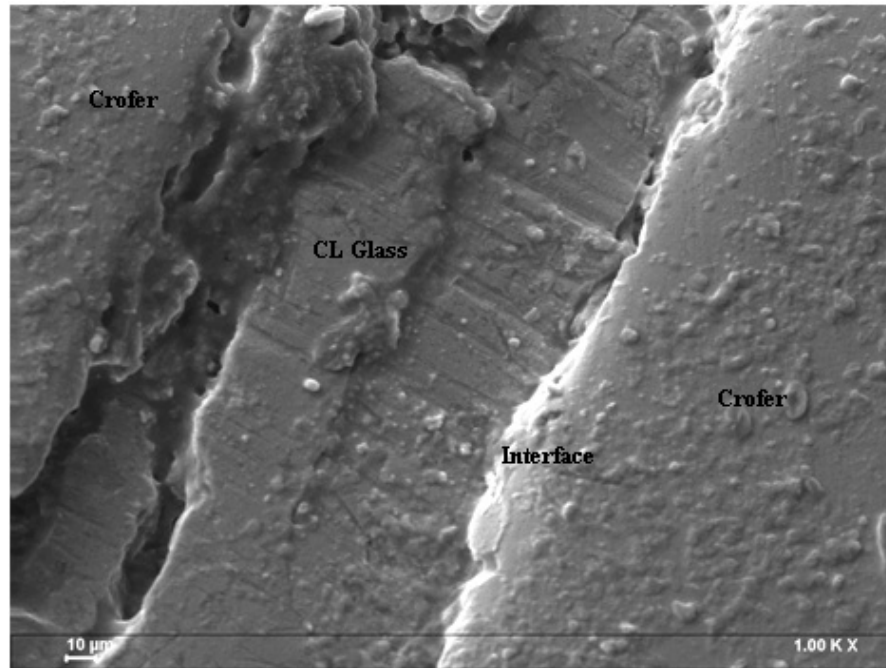


Figure 4.21 (a): Crofer 22APU/CL/Crofer 22APU diffusion couple at 850 °C for 750 h.

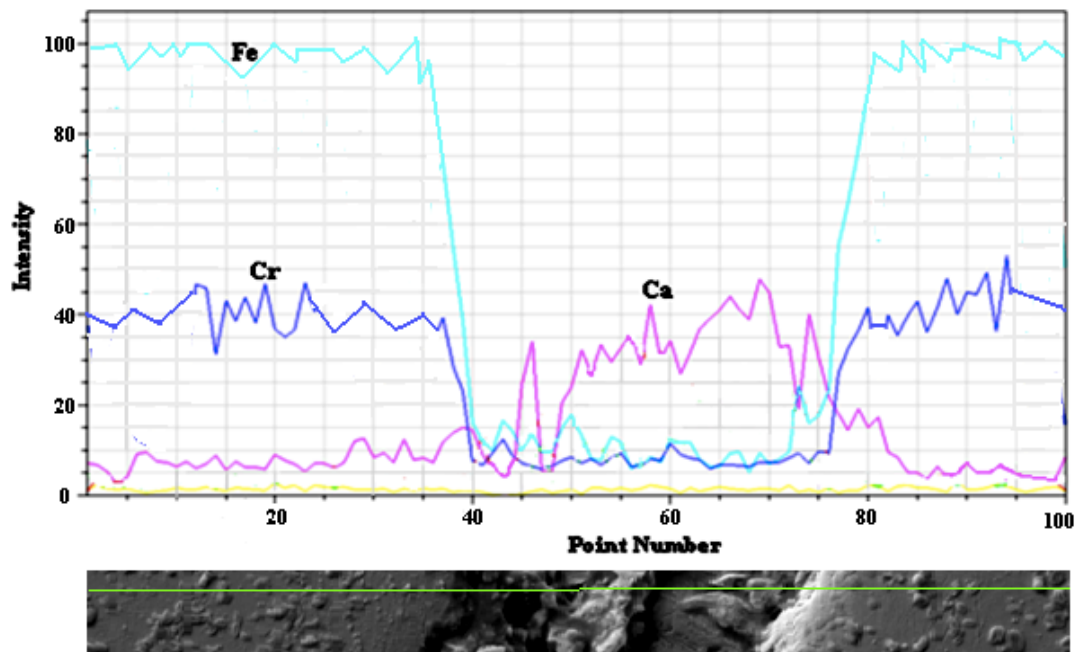


Figure 4.21 (b): EPMA line scan of joint region shown in fig. 4.21(a).

For Crofer 22APU/CL/Crofer 22APU couple (heat-treated at 850 °C for 750 h), a very good adhesion is achieved as shown in fig. 4.21(a). The interface is devoid of cracks. The interface does not exhibit any substantial change because of absence of any interaction products. The chromium and iron diffusion has also been considerably low as is clear from the EPMA (fig. 4.21(b)). The diffusion content was quite low for these cations from the glass. No undesired reaction took place at the interface completely precluding the absence of any corrosion products at the interface. Fig. 4.21(c) shows the microstructure of coupled CL glass heat-treated at 850 °C for 750 h. The activation energy of CL glass is small, hence the crystallized fraction is higher in this glass and as reported, crystallization is beneficial for attaining mechanical strength [72]. Hence CL glass seal coupled between interconnect plates and heat-treated at 850 °C for 750 h provided high gas tightness along with high hermeticity.

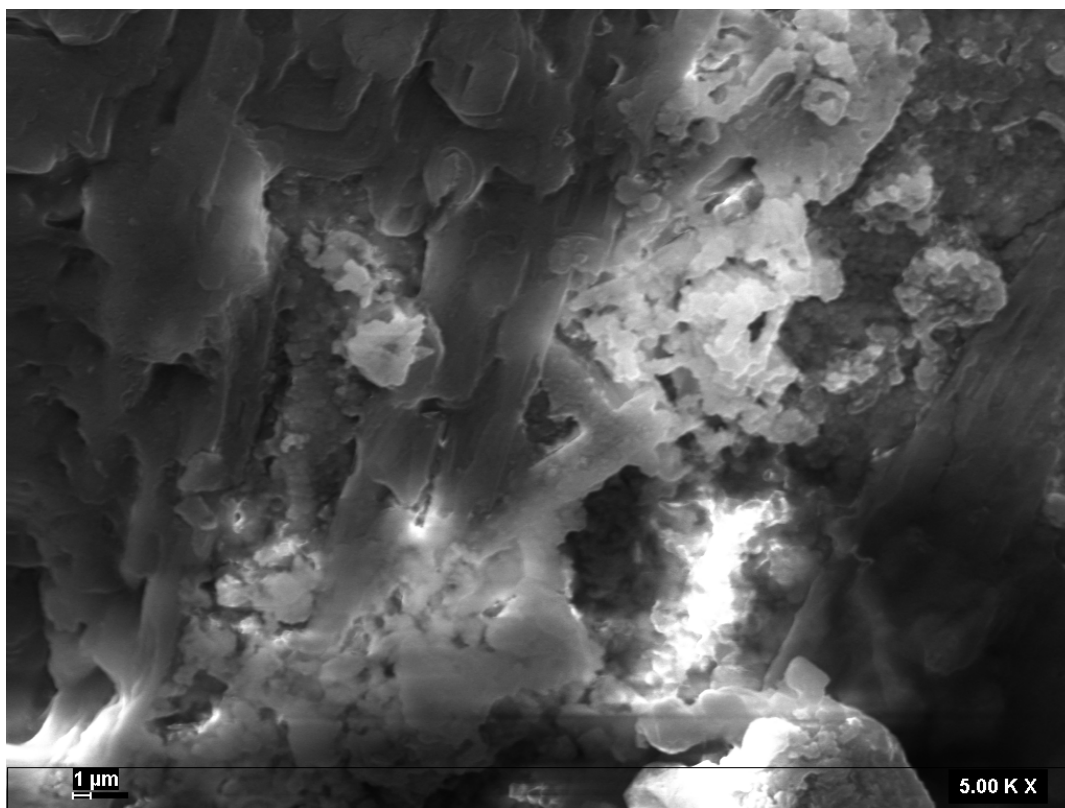


Figure 4.21(c): Microstructure of coupled CL glass-ceramic between Crofer plates after heat-treatment of 750 h.

4.2.2.3 SL/ Crofer 22APU couple: Fig. 4.22 (a) shows the diffusion couple of SL/Crofer 22APU heat-treated at 850 °C for 5 h in air. Examination around the seal region shows a very good adhesion between SL glass and ferritic interconnect Crofer 22APU. The interface is

continuous and devoid of pores and cracks. The origin of cracks at the interface is mostly due to devitrification. Devitrification causes CTE mismatch between glass phase and devitrified phase decrease in glass volume and poor gas flow at interface. From the morphological point of view, no structural modifications leading to formation of cracks are observed at the joint region. As is evident from elemental mapping (fig. 4.22 (b)), the interface is free from iron rich oxide products but chromium has diffused to a considerable extent. Diffusion of Sr^{2+} is also seen on either side of interface. Fig. 4.23 (a) shows the interface of SL/ Crofer 22APU couple heat-treated at 850 °C for 100 h. After 100 h treatment the interface remains intact and is free from cracks and gaps. A strong metal-glass seal bond is observed at the interface without showing any detrimental reaction products. From elemental mapping of couple (fig. 4.23 (b)), it could be observed that the presence of chromium is less as compared to SL/ Crofer 22APU couple heat-treated for 5 h. The chromium rich layer at the interface is presumably due to dissolution of Cr from the crofer to glass ceramic.

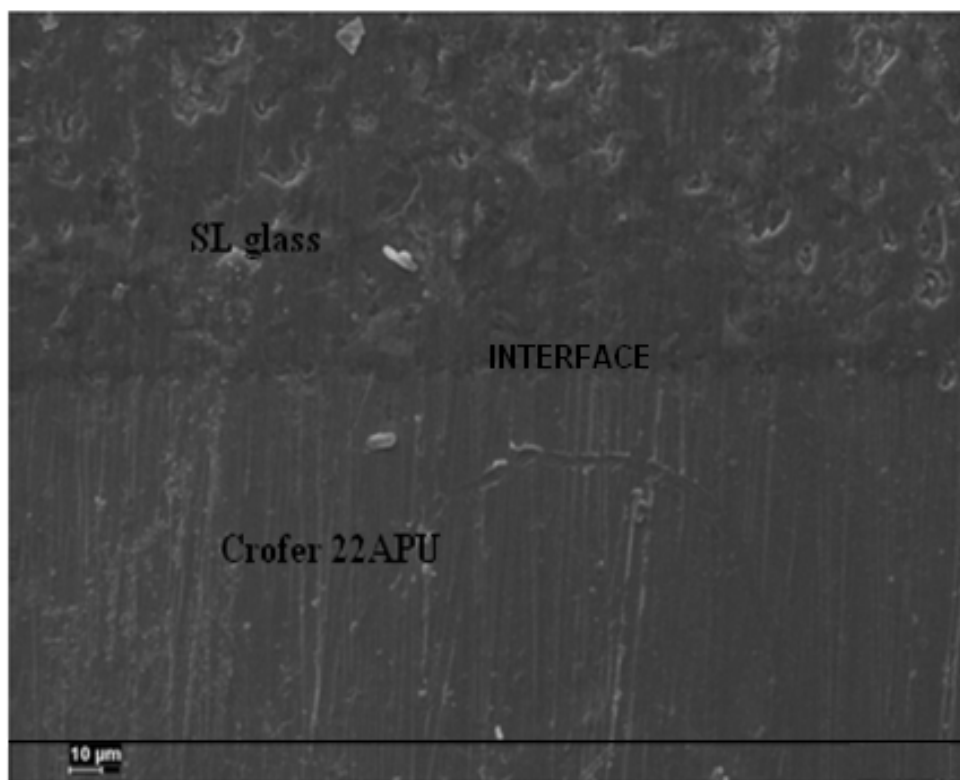


Figure 4.22(a): SL/ Crofer 22APU diffusion couple at 850 °C for 5 h.

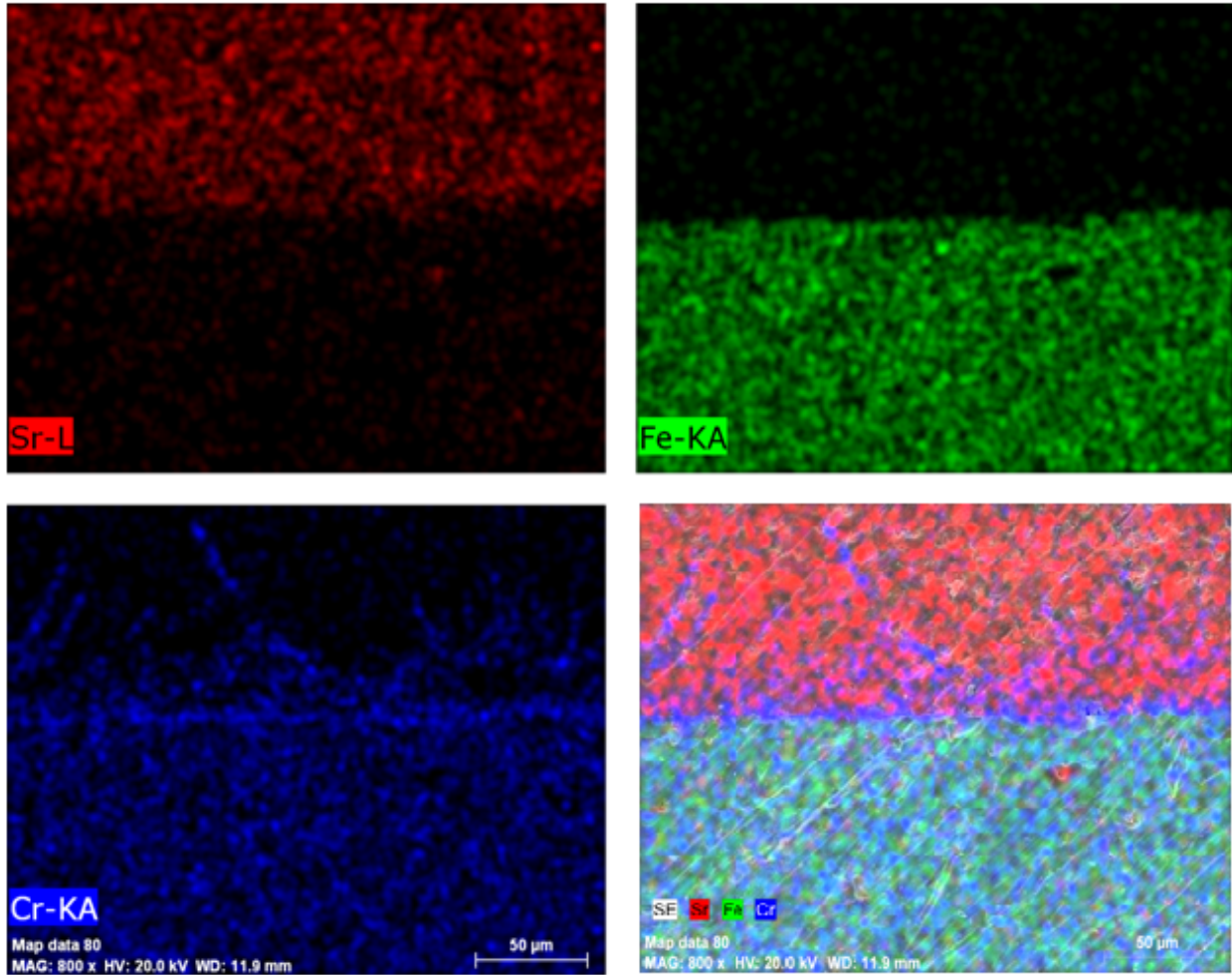


Figure 4.22 (b): X-ray dot mapping of SL/Crofer 22APU diffusion couple at 850 °C for 5 h.

Even after prolonged heat treatment of 750 h at 850 °C, the interface region of SL/Crofer 22APU (fig. 4.24 (a)) is very smooth. SL glass seal is well adhered to the interconnect Crofer 22APU and exhibiting good bonding characteristics. However, some pits could be seen at the central part of glass which could be due to the volatility of entrapped gases during the process of glass formation. The absence of unwanted reaction products especially chromates further confirmed the stability of glass seals (fig. 4.24(b)).

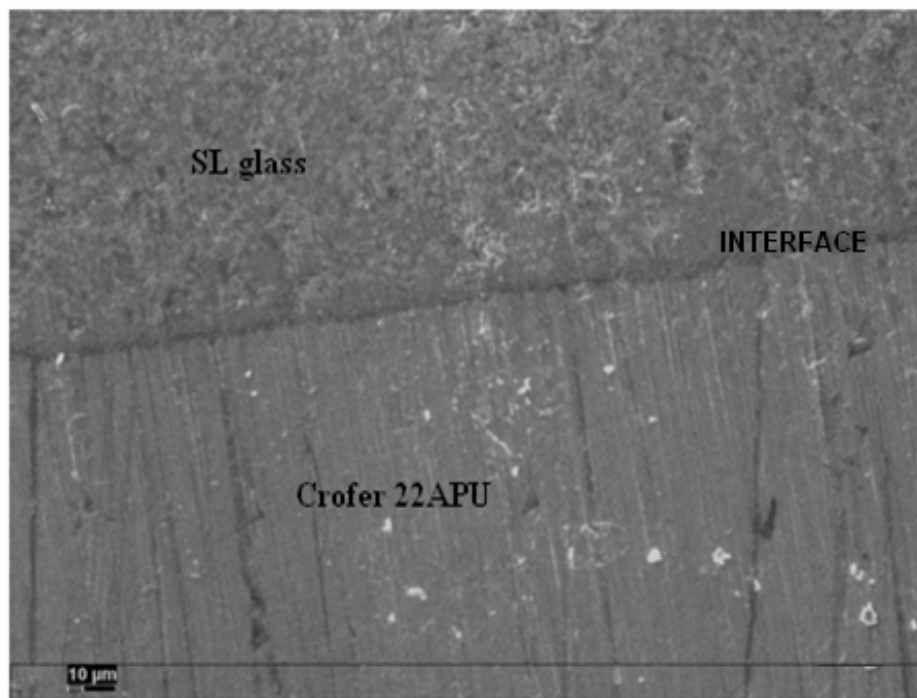


Figure 4.23 (a): SL/Crofer 22APU diffusion couple at 850 °C for 100 h.

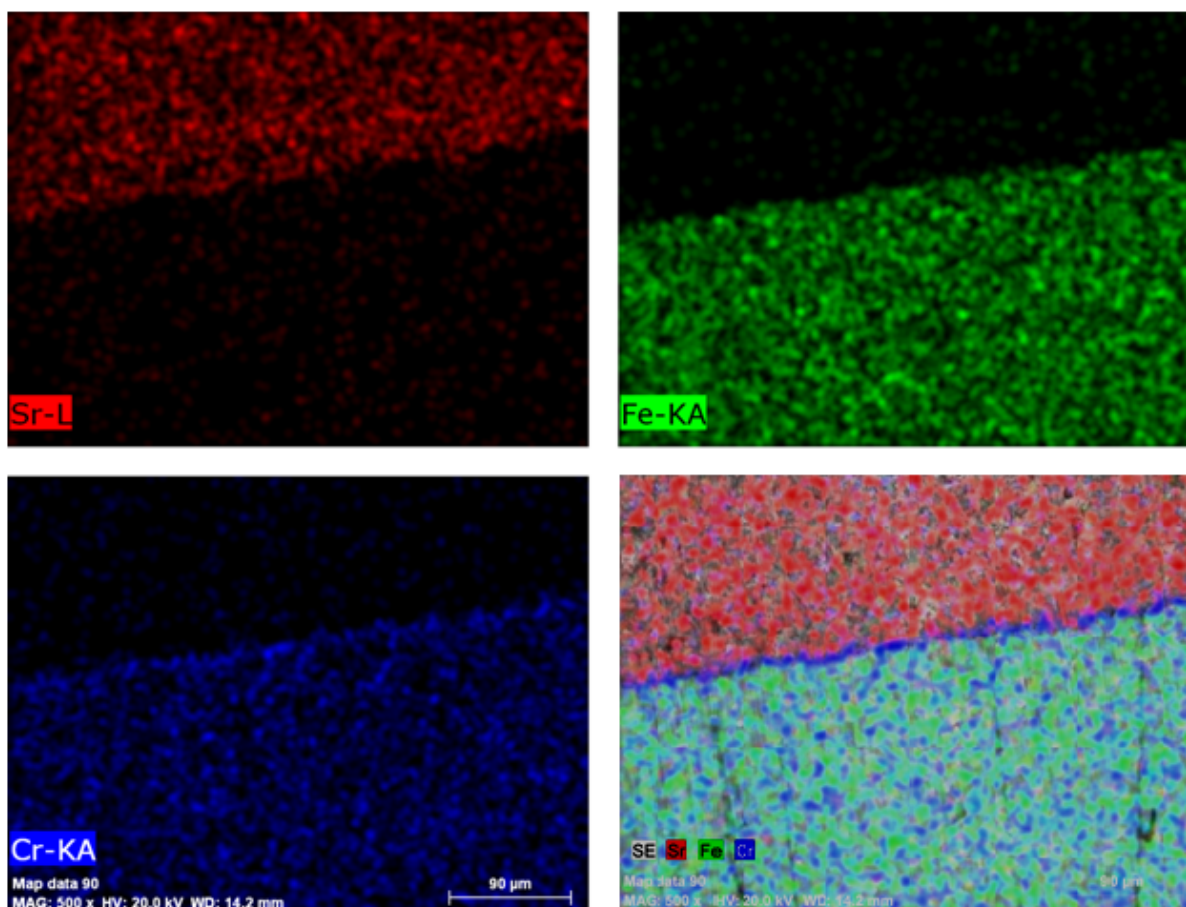


Figure 4.23 (b): X-ray dot mapping of SL/Crofer 22APU diffusion couple at 850 °C for 100 h.

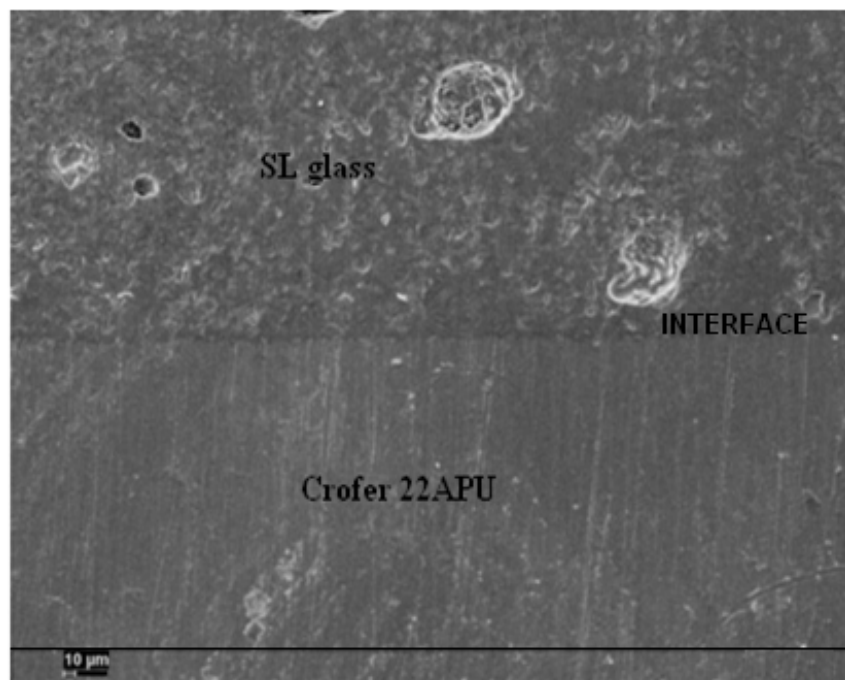


Figure 4.24 (a): SL/Crofer 22APU diffusion couple at 850 °C for 750 h.

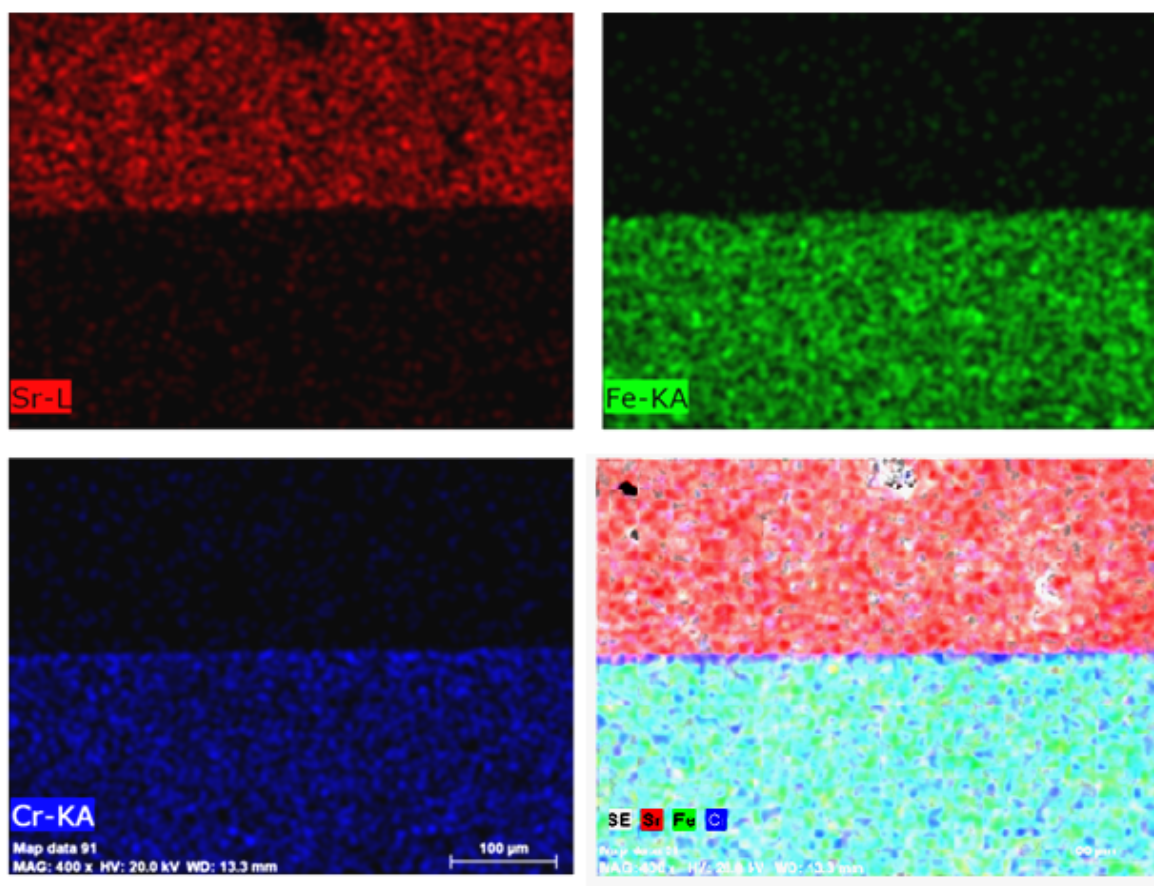


Figure 4.24 (b): X-ray dot mapping of SL/Crofer 22APU diffusion couple at 850 °C for 750 h.

Fig. 4.25 shows the microstructure of devitrified coupled glass seal after 750 h treatment. Two crystalline phases are present in the residual glass. SrSiO_3 is seen as white long elongated crystals growing in amorphous glass. The dark needle shaped crystals of Sr_2SiO_4 also grew in glass matrix. As the duration of heat-treatment increased from 5 h to 750 h, the extent of chromium diffusion decreased. This phenomenon might be explained as follows:

(a) Chromium diffusion towards either side of interface is fast initially due to larger concentration gradient between glass seal and Crofer 22APU. Moreover, the ionic radius of chromium is very small as compared to iron and other cations, which sustains its fast diffusion kinetics.

(b) The functional dependence of diffusion coefficient (D) on time (t) is given by parabolic law of oxidation [43] i.e.

$$D = x^2/t \quad (4.35)$$

where x is the interphase thickness. This relation clearly implies the decrease in diffusion with increase in time duration of heat-treatment, which goes in accordance with experimentally, obtained results. During prolonged heat-treatment of the sample, other cations like lanthanum and iron also migrate towards either side of interface to some extent. The diffusion kinetics for heavy metal ions is very slow as they tend to remain in the glassy phase and hence the movement of ions is restricted.

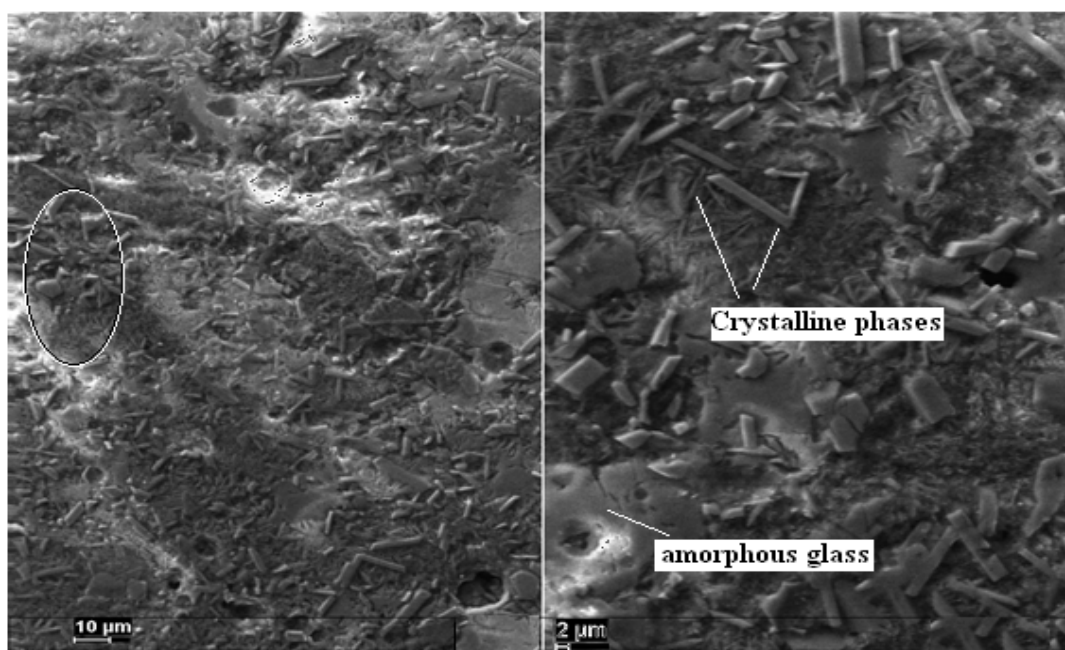


Figure 4.25: Microstructure of coupled SL glass-ceramic between Crofer 22APU plates after heat-treatment of 750 h.

4.5.2.4 BL/ Crofer 22APU: Fig. 4.26 (a) shows the interfacial region of BL glass seal and Crofer 22APU interconnect heat-treated at 850 °C for 5 h. No delamination or reaction zone at the interface is seen. At both the edge and inside area, the sealing glass ceramic BL is well bonded to Crofer 22APU. Unlike SL/ Crofer 22APU diffusion couples, no chromium rich layer is observed though some penetration of Cr, Fe and Ba on either side of interface is evident from elemental mapping (fig. 4.26 (b)). Fig. 4.27 (a) shows BL/ Crofer 22APU couple heat-treated at 850 °C for 100 h. No porosity, undesired reactions or corrosion products are found at the joint sealing region. However, some residual porosity could be seen in the glass region. The shape of the pores indicates that these have formed due to formation of vapor species. These vapour species are created mostly via the interaction of alloy elements especially chromium with dissolved water or alkaline oxide residues in the glass [55]. Electron probe microanalysis (EPMA) along the interface region indicates higher diffusion of chromium than iron into glass-ceramic. It is well reported in literature that chromium is more volatile than other species [73-75]. The line profile of elemental variation along the interface is shown in fig. 4.27 (b). The concentration profiles observed along glass to Crofer are S-shaped (shape followed in EPMA) as reported by Mahapatra et.al. [76].

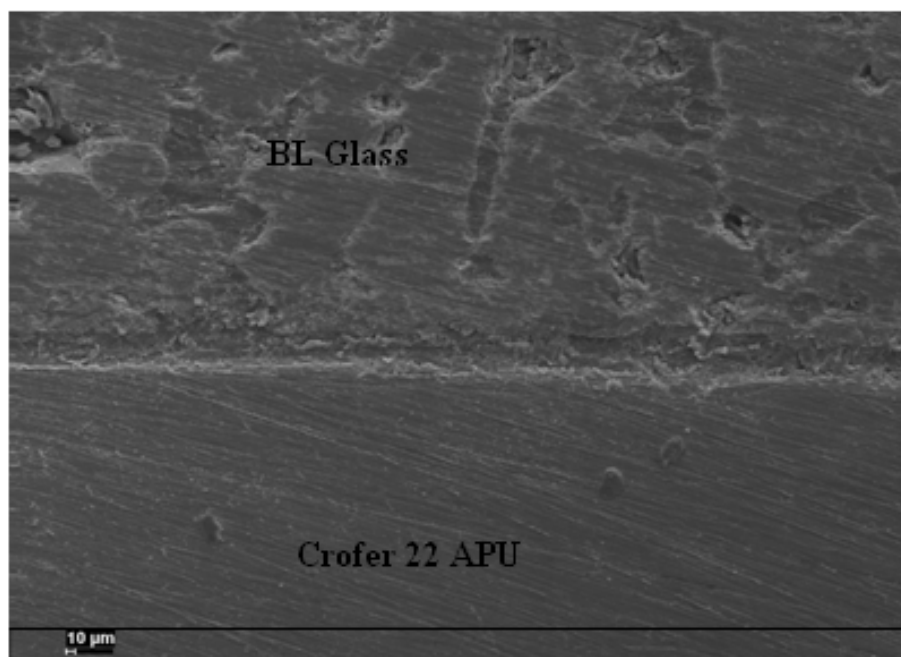


Figure 4.26 (a): BL/ Crofer 22APU diffusion couple at 850 °C for 5 h.

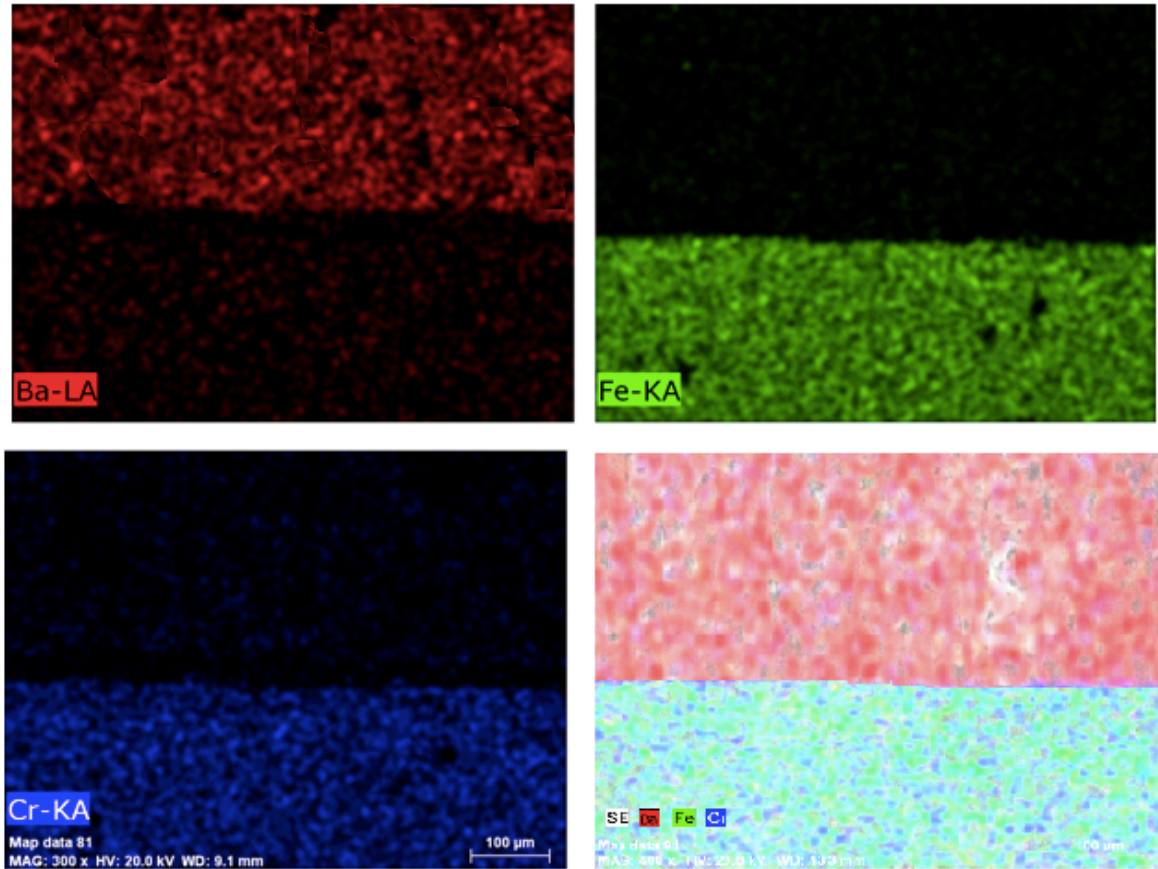


Figure 4.26 (b): X-ray dot mapping of BL/ Crofer 22APU diffusion couple at 850 °C for 5 h.

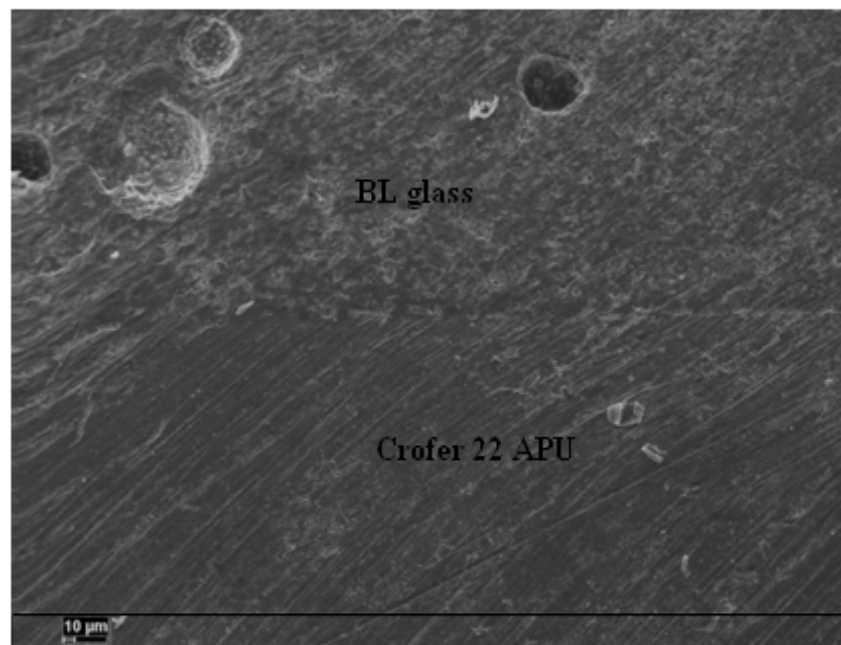


Figure 4.27 (a): BL/Crofer 22APU diffusion couple at 850 °C for 100 h.

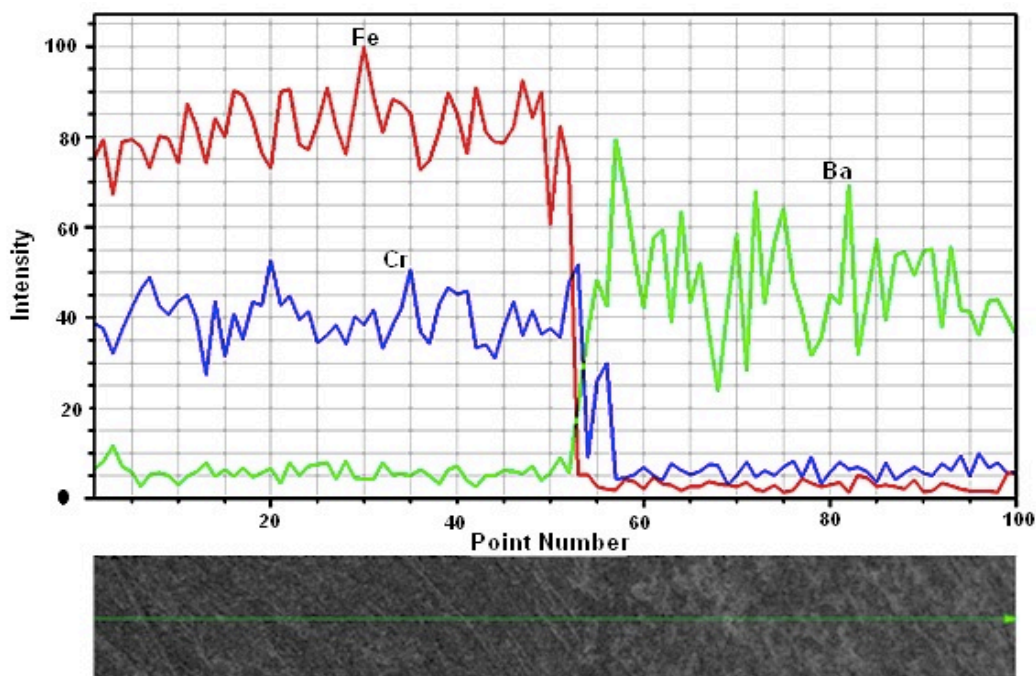


Figure 4.27 (b): EPMA of BL/ Crofer 22APU diffusion couple at 850 °C for 100 h.

Oscillations are observed in the concentration profiles for all elements. Several possible reasons are given for that i.e. low density and concentration of glass elements, compositional difference between devitrified and glassy phase and interaction between X-rays of different elements [77]. The chromium concentration profile clearly indicates its high presence at the interface. Each curve represents the relative distribution of a specific element but not the absolute content of the system. Fe diffuses in a homogenous and more regular pattern as beyond the interface, the spikes are absent in the line profile. This could likely result in the formation of strong bonding between the glass ceramic BL and Crofer 22APU via mechanical interlocking [71].

For 750 h heat-treated BL/Crofer 22APU diffusion couple at 850 °C, the extent of closed pits increased though the interfacial adhesion is very good and still free from cracks (fig. 4.28(a)). In the interior region of the interface, the microstructure is very different from the edge area. The pits are homogeneously distributed in the glass ceramic. Besides larger pits, a population of smaller pores was also seen surrounding them. The appearance of closed porosity (pits) is a usual phenomenon and does not lead to enhancement of leak rate for the final seal [78]. No unusual elemental segregation was identified at the glass ceramic surrounding the pores. However, the presence of pores and enhancement in their volume fraction for BL glass is more than SL glass.

There was no accumulation of unwanted crystalline phases at the interface as is clear from elemental analysis (fig. 4.28(b)).

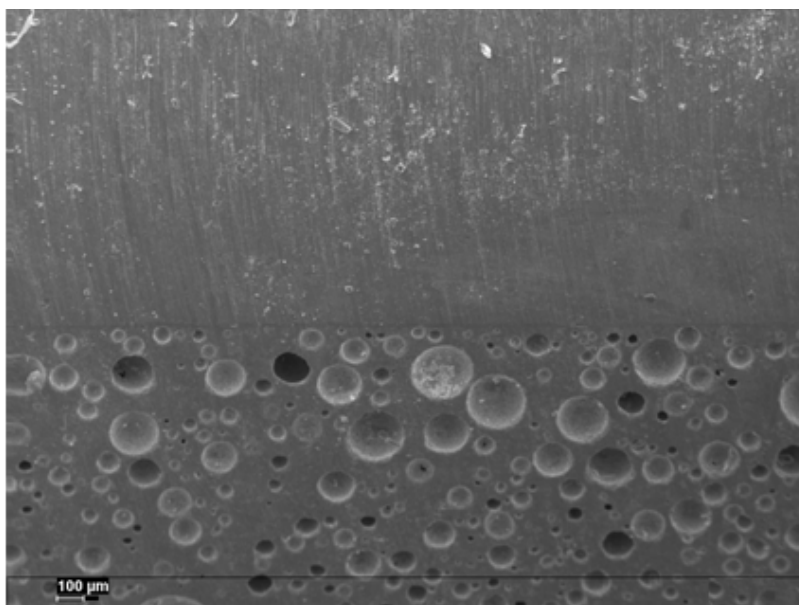


Figure 4.28 (a): BL/Crofer 22APU diffusion couple at 850 °C for 750 h.

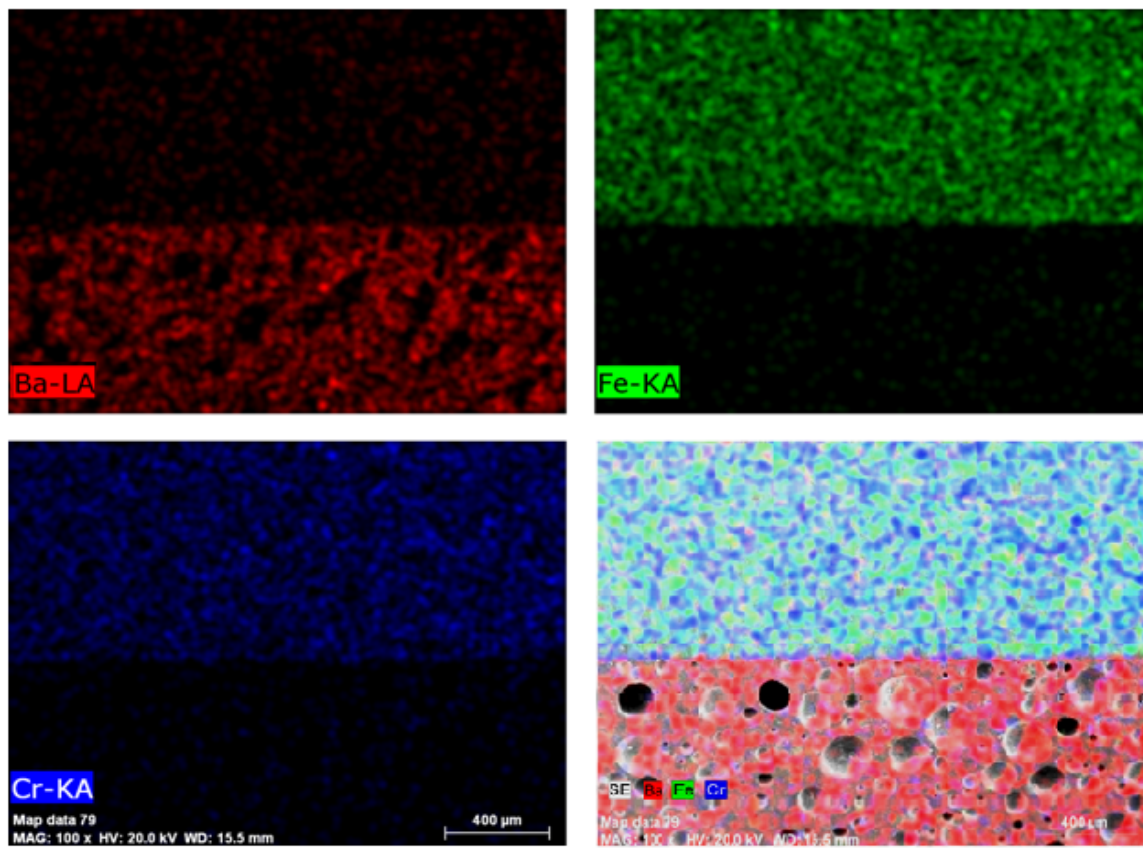


Figure 4.28 (b): X-Ray dot mapping of BL/Crofer 22APU diffusion couple at 850 °C for 750 h.

The ceramic phases being brittle cannot withstand tensile stresses and therefore lead to crack formation. Fig. 4.29 demonstrates the magnified image of the biggest closed pore (area= 41247 μm^2 , $d= 0.23 \text{ mm}$) observed in BL/Crofer 22APU (heat-treated at 850 °C for 750 h).

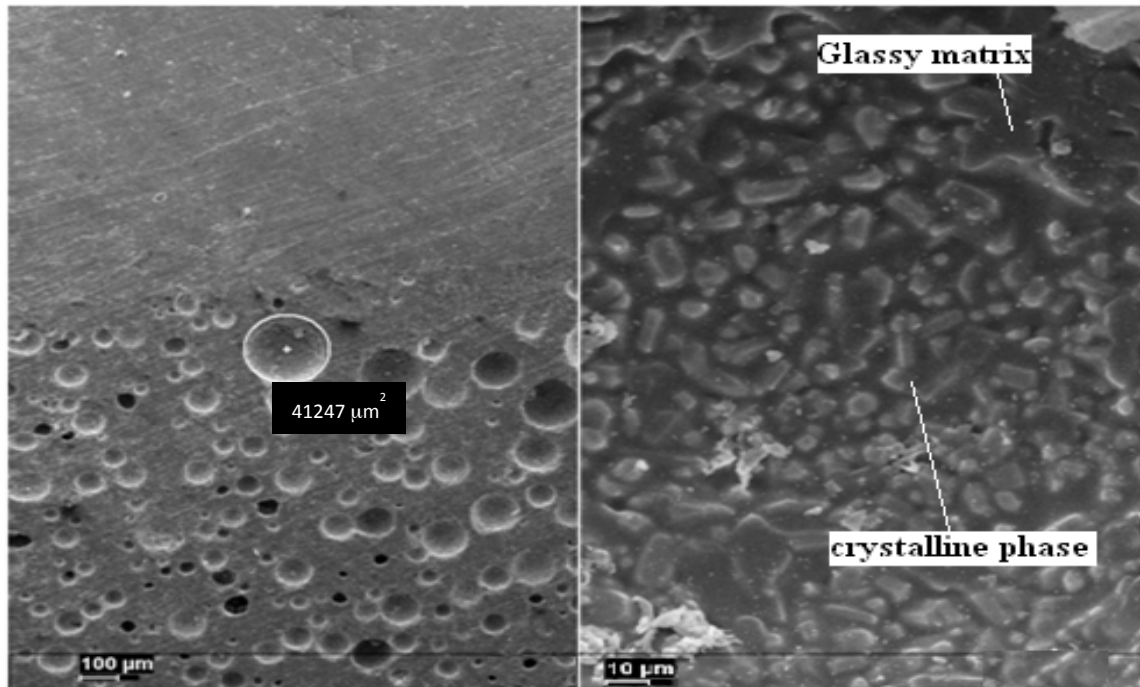


Figure 4.29: Magnified image of closed porosity for coupled BL glass seal after 750 h treatment.

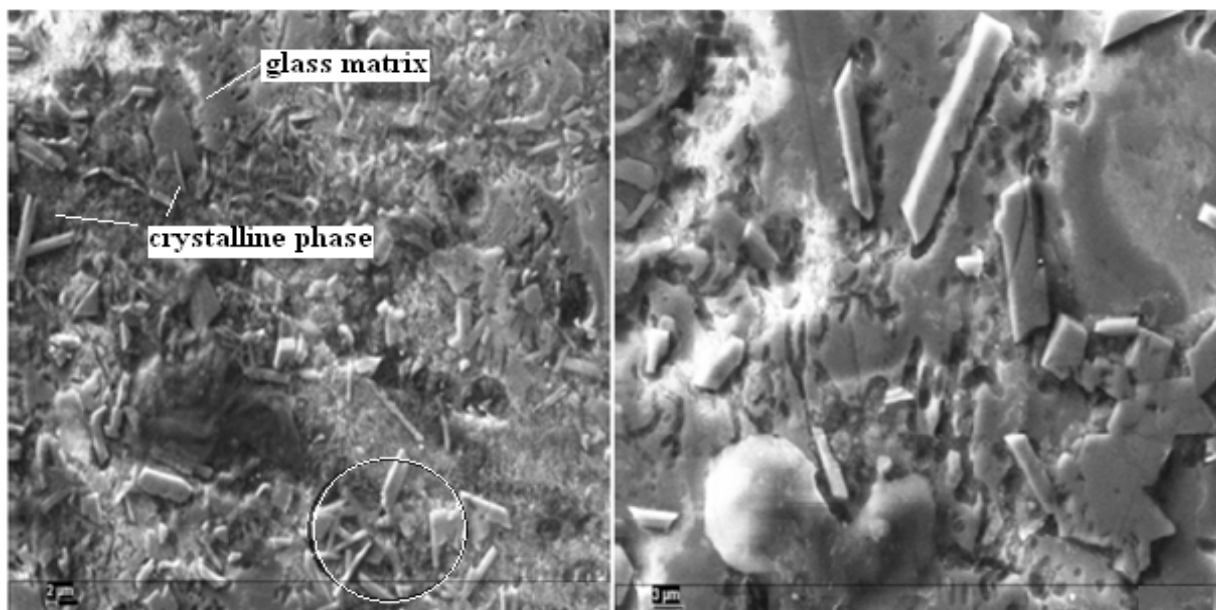


Figure 4.30: Microstructure of coupled BL glass-ceramic between Crofer 22APU plates after 750 h heat-treatment.

The microstructure within the pit signifies the crystalline phase embedded in amorphous glassy matrix. Fig. 4.30 shows the SEM micrograph of BL coupled glass heat treated at 850 °C for 750 h clearly indicate the emergence of two crystalline phases in the glass. BaSiO_3 is observed as thin needles like crystals growing in amorphous glass. The rod shaped crystals of Ba_2SiO_5 also grew in amorphous glass matrix. The results are in well agreement with those obtained from the X-ray diffraction. Based on XRD results and microstructural analysis, it can be concluded that both the sealants do not form any detrimental crystalline phases. Absence of these detrimental phases, such as chromate phase and iron chromium rich phase indicate that both the glasses may work as a sealant in real SOFC condition.

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CHAPTER 5

RESULTS AND DISCUSSION-II

Overview

In the present study, the bonding and sealing behavior of RO-B₂O₃-SiO₂-La₂O₃ [R = Mg, Ca, Sr, Ba] glass seals and high temperature electrolyte (yttria-stabilised zirconia-YSZ) as well as intermediate temperature electrolyte i.e. titanium doped bismuth vanadate Bi₂V_{0.80}Ti_{0.2}O_{5.5-δ} (TBV) has been investigated. The prepared couples has been thoroughly studied as a function of different heating durations of 5, 100 and 750 h using X-ray diffraction (XRD), scanning electron microscopy (SEM), electron-probe microanalysis (EPMA) and X-ray dot mapping techniques. Titanium doped bismuth vanadates (TBV) have been viewed as promising electrolyte for low to intermediate temperature solid oxide fuel cells (IT-SOFC). The phase transition behavior, thermal analysis, expansivity and conductive behavior have been studied for Bi₂V_{1-x}Ti_xO_{5.5-δ} (0.05 ≤ x ≤ 0.20) in order to obtain the best conducting sample with desirable CTE. TBV have shown good conductivity along with thermal stability at 800 °C.

5.1 Synthesis of titania doped bismuth vanadate (TBV)

For intermediate temperature solid oxide fuel cell (IT-SOFC), bismuth vanadate $\text{Bi}_2\text{V O}_{5.5-\delta}$ is a favourable oxygen ion electrolyte conductor exhibiting aurivillius structure [1-3]. It is known that doping at vanadium site changes the phase transformation behavior as well as electrical conductivity in BIMEVOX systems [5-8]. The compounds BIMEVOX (where BI represents bismuth, ME represents the dopant ion, V is the vanadium atom and OX represents oxygen) is the combined depiction of a large family of compounds where ME can be Cu, Ni, Ti, Pb, Zn, Fe, Al, Sb and Nb etc. are used to increase the ionic conductivity by stabilizing γ phase at room temperatures [8-14]. Aliovalent doping is expected to change the amount of oxygen vacancy to preserve electroneutrality of the system. Moreover, the variation of size between vanadium and dopant induces lattice strain in BIMEVOX structure. The affinity between dopant and oxide ion can be described by lattice energy Q which is given by negative value of enthalpy change as per following reaction:



Dopant, which exhibits high Q value, binds more strongly with the oxide ion in BIMEVOX. These affinities between the atoms, which are influenced by the synthesis conditions, play a crucial role in determining the conductive properties and phase stabilization [1, 10-15]. The phase transition behavior, thermal analysis, expansivity and conductive behavior have been studied for $\text{Bi}_2\text{V}_{1-x}\text{Ti}_x\text{O}_{5.5-\delta}$ ($0.05 \leq x \leq 0.20$). Ti^{3+} exhibits six-fold octahedron having ionic radii of $0.67\text{\AA}$ along with very high lattice energy of 14.15 MJ/mol [16]. In contrast to this, Ti^{4+} has ionic radii of $0.605\text{\AA}$ and lattice energy 12.01 MJ/mol . Vanadium V^{5+} exhibits ionic radii of $0.054\text{\AA}$ and lattice energy of 19.24 MJ/mol . Therefore, Ti_2O_3 has been chosen as an initial ingredient instead of TiO_2 due to its high lattice energy. Moreover, CTE as well as other thermal parameters has been given wide consideration, as they are very important from the SOFC point of view. The best electrolyte is chosen for further interaction study with glasses.

5.1.1 X-ray diffraction (XRD)

The XRD pattern of $\text{Bi}_2\text{V}_{1-x}\text{Ti}_x\text{O}_{5.5-\delta}$ ($0.05 \leq x \leq 0.25$) has been shown in fig. 5.1(a). XRD data confirmed the presence of single phase in all samples except for $x = 0.25$. $\text{Bi}_2\text{V}_{0.75}\text{Ti}_{0.25}\text{O}_{5.5-\delta}$ oxide exhibited double phase i.e. BiVO_4 phase precipitated and $\text{Bi}_2\text{V}_{0.75}\text{Ti}_{0.25}\text{O}_{5.5-\delta}$ phases. BiVO_4 is a mixed conductor of electrons and oxide ions [17].

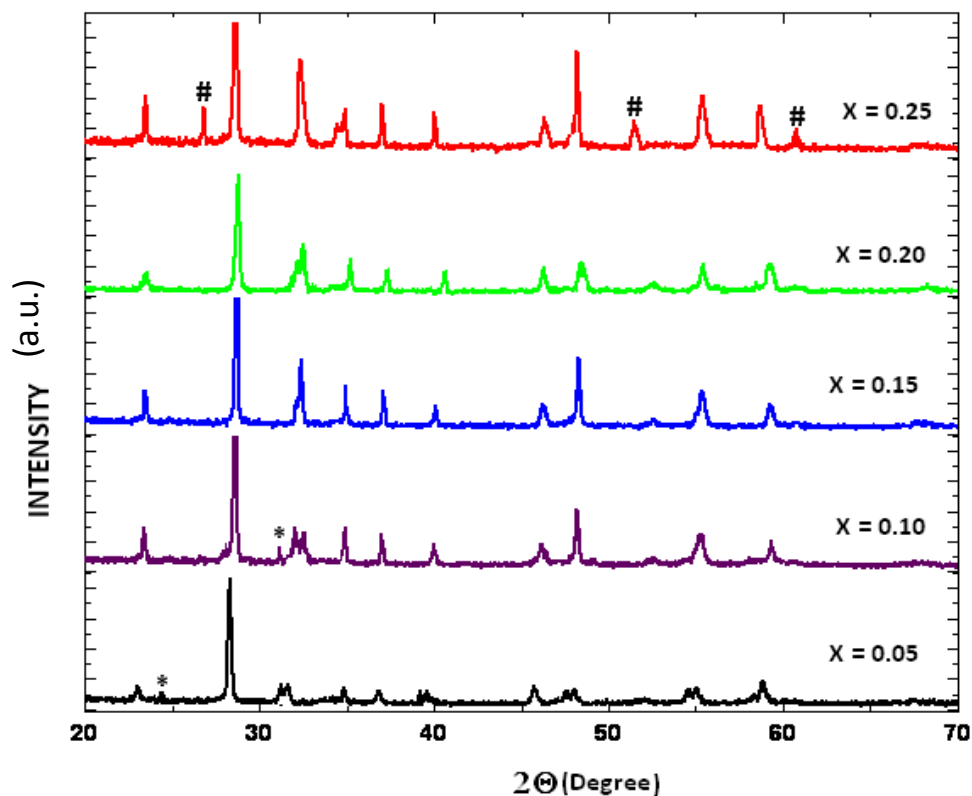


Figure 5.1 (a): XRD spectrum obtained for the samples $\text{Bi}_2\text{V}_{1-x}\text{Ti}_x\text{O}_{5.5-\delta}$ ($0.05 < x < 0.25$) [* - superlattice reflection, #- BiVO_4 phase].

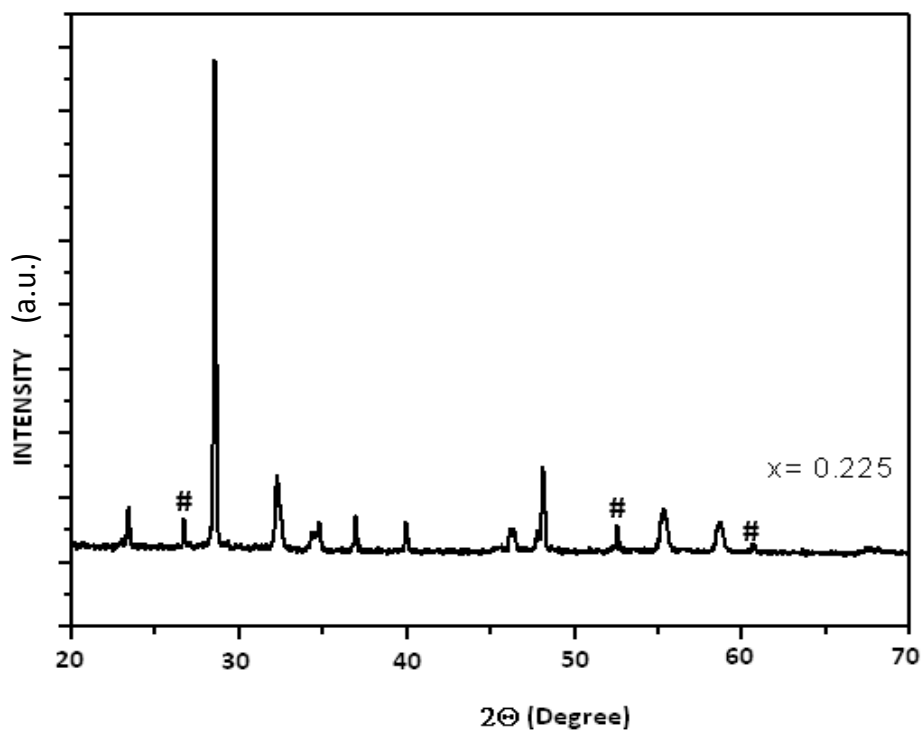


Figure 5.1 (b): XRD spectrum obtained for the sample $x = 0.225$ [# - BiVO_4 phase].

During long-term operation of SOFC, electronic conduction can lead to short-circuit. As the interest of present study is more focused on obtaining single phase, hence further investigation of $\text{Bi}_2\text{V}_{0.75}\text{Ti}_{0.25}\text{O}_{5.5-\delta}$ oxide was not done. In order to detect more precise solid solubility limit, $\text{Bi}_2\text{V}_{0.775}\text{Ti}_{0.225}\text{O}_{5.5-\delta}$ sample was also synthesized and characterized using XRD. This sample also exhibited mixed phase as indicated by X-ray diffractogram shown in fig. 5.1(b). This further confirms the solid solubility limit upto $x = 0.2$. For $x = 0.05$ sample, the diffraction pattern is characterized by the presence of weak reflection at $2\Theta = 24.22^\circ$. In addition to this, doublets have also been observed at $2\Theta = 31^\circ, 39^\circ, 48^\circ$ and 54° which clearly indicate the presence of α phase in this sample [2, 18]. The XRD pattern of $x = 0.1$ shows the presence of two superlattice peaks at $2\Theta = 31.8^\circ$ and 32.4° (with splitting). This further confirms the existence of β phase for $x = 0.1$ [19-20]. On the other hand, $x = 0.15$ and 0.2 , the XRD pattern does not show any superlattice diffraction peaks confirming the presence of γ phase in these samples [21]. Along with this, the shift in peaks has also been observed towards higher diffraction angles with the increase in dopant concentration, which could be attributed to the strain induced in lattice. For $x = 0.25$, the shift of peaks have occurred towards lower diffraction angle. For further confirmation of γ - phase stabilization, heating and cooling cycles of DTA was performed. The results are discussed in the following section.

5.1.2 Differential thermal analysis (DTA)

DTA was performed in order to determine the phase transformations during thermal cycling and to check their stability in such conditions. Figure 5.2(a-d) shows the DTA profiles and differential DTA of all samples along with their weight change (as shown in inset) during heating and cooling cycle. For $x = 0.05$ sample (fig. 5.2(a)), two endothermic peaks at 418°C and 529°C have been observed during heating cycle. The peak at 418°C corresponds to transition from α to β phase (α/β) whereas endotherm at 529°C represents phase transition from β to γ phase (β/γ) [22]. The exothermic peaks at 409°C and 512°C during cooling cycle correspond to phase transition from β to α phase (β/α) and γ to β phase (γ/β), respectively. The transition temperatures are determined from the onset temperatures of endo-exothermic peaks. The transition temperatures have shifted to lower side during cooling cycle. The peak positions obtained from differential DTA are also in correlation with the peak positions obtained from DTA during heating and cooling cycles. Differential method is advantageous as it allows peak

detection even in the case of raw data as well as in the case of a peak overlapped with another peak at its shoulder, thus making its detection difficult sometimes.

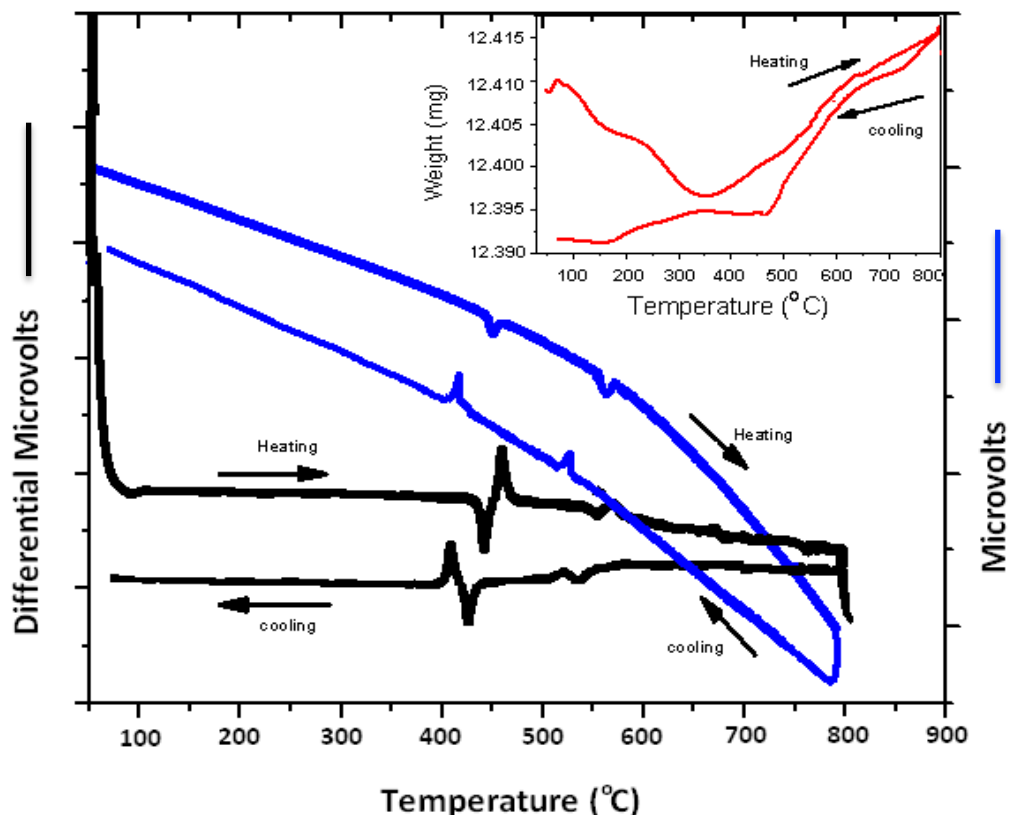


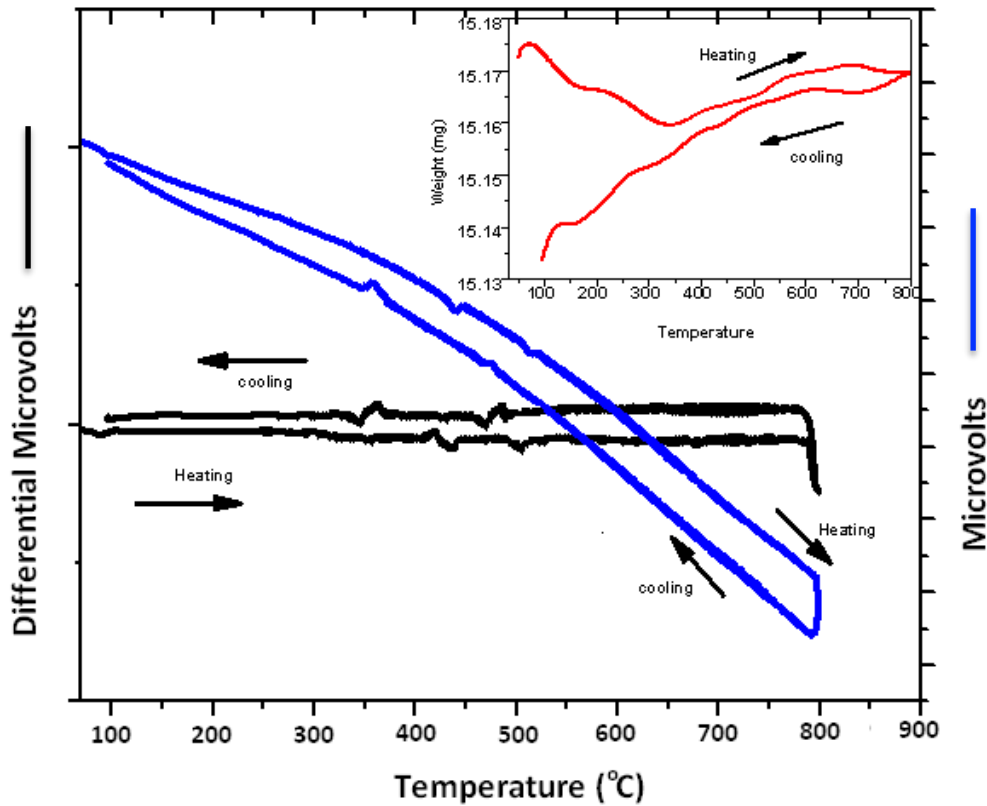
Figure 5.2 (a): DTA, TGA and differential DTA for the sample $x = 0.05$.

Moreover, the data obtained has baseline correction, which makes the detection of peaks easy. The weight change has been shown in the inset of fig. 5.2(a) for sample $x = 0.05$. During heating, the first step occupies the region from room temperature till 340 °C for which the weight loss occurred is attributed to the humidity. The second region from 340 °C to 800 °C has an abrupt increase in weight, which could be due to partial oxidation of different ions. During cooling, the first region of temperature from 800-480 °C at which weight loss occurred can be due to partial reduction of ions. The second region occupying the range 480-120 °C is due to full reduction of ions as well as the final formation of solid-state oxide [24-25]. Weight change is attributed basically to the change in oxygen content. The change in oxygen content from TGA has been calculated and listed in table 5.1 for all the studied samples.

Table 5.1: Oxygen disorder in samples with heating or cooling.

Sample name	Heating	Cooling
$\text{Bi}_2\text{V}_{0.95}\text{Ti}_{0.05}\text{O}_{5.5-\delta}$	$\text{Bi}_2\text{V}_{.95}\text{Ti}_{.05}\text{O}_{5.509}$	$\text{Bi}_2\text{V}_{.95}\text{Ti}_{.05}\text{O}_{5.475}$
$\text{Bi}_2\text{V}_{0.90}\text{Ti}_{0.10}\text{O}_{5.5-\delta}$	$\text{Bi}_2\text{V}_{.90}\text{Ti}_{.10}\text{O}_{5.493}$	$\text{Bi}_2\text{V}_{.90}\text{Ti}_{.10}\text{O}_{5.469}$
$\text{Bi}_2\text{V}_{0.85}\text{Ti}_{0.15}\text{O}_{5.5-\delta}$	$\text{Bi}_2\text{V}_{.85}\text{Ti}_{.15}\text{O}_{5.477}$	$\text{Bi}_2\text{V}_{.85}\text{Ti}_{.15}\text{O}_{5.467}$
$\text{Bi}_2\text{V}_{0.80}\text{Ti}_{0.20}\text{O}_{5.5-\delta}$	$\text{Bi}_2\text{V}_{.80}\text{Ti}_{.20}\text{O}_{5.449}$	$\text{Bi}_2\text{V}_{.80}\text{Ti}_{.20}\text{O}_{5.456}$

During heating the sample has been oxidized whereas during cooling the sample has been reduced. For $x = 0.1$, the transitions has been observed at 432 °C (α/β) and 518 °C (β/γ) during heating as is clear from fig. 5.2(b). During cooling cycle, the transition onset temperatures have shifted to 478 °C (γ/β) and 367 °C (β/α), respectively. In addition to this, the sharpness of peaks reduced in comparison to $x = 0.05$. Broad and small peaks represent continuous conductivity change (shown later).

**Figure 5.2 (b):** DTA, TGA and differential DTA for the sample $x = 0.1$.

γ phase is stabilized against α and β with the widening of temperature region for γ as is indicated by the shift in phase transition points toward lower temperature during cooling cycle. For $x = 0.15$ and 0.2 , γ is stabilized at room temperature as depicted by fig. 5.2(c-d).

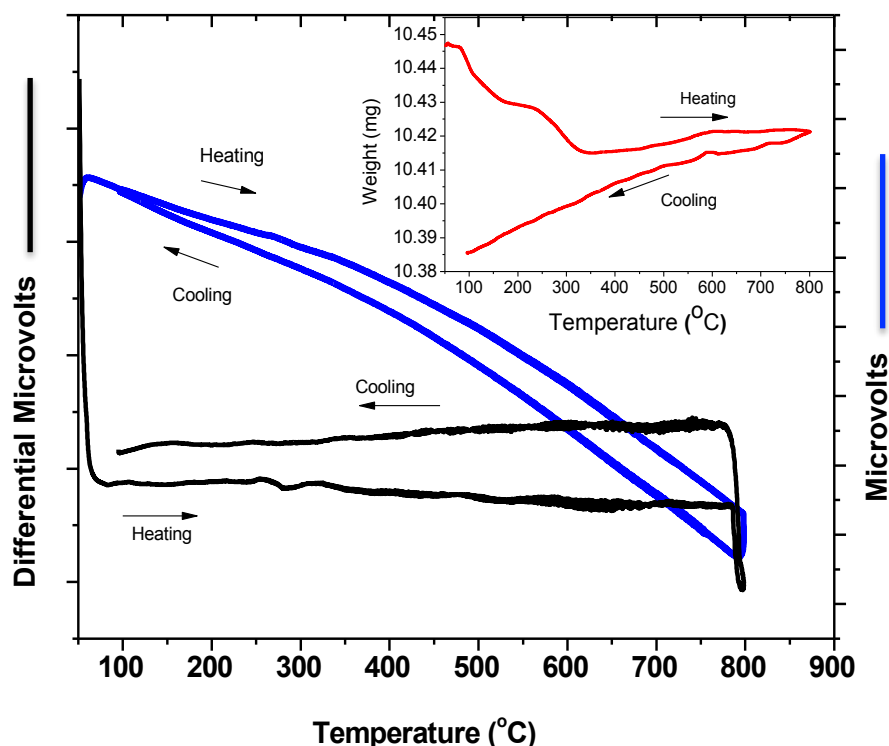


Figure 5.2 (c): DTA, TGA and differential DTA for the sample $x = 0.15$.

Both the samples show no evidence of (α/β) or (β/γ) transitions during heating or cooling cycle. Doping on V site increases the configurational entropy due to crystallographic distortion [1]. This has an advantage to thermodynamically stabilizes γ phase against β or α phase in $\text{Bi}_2\text{VO}_{5.5-\delta}$. Hence, presence of large amount of oxygen vacancies due to dopant in V-O layers retards the ordering from γ to β or α phase. For $x = 0.15$, a small inflection is observed at about 258 °C during heating cycle which could be due to some structural relaxation induced by the rearrangement of oxygen vacancies [15, 19]. From table 5.1, it is very clear that the disorder in oxygen is increasing with dopant concentration during heating and cooling cycle. Moreover, all the samples have shown reduction during the cooling cycle as is indicated by the weight change. Therefore Ti^{3+} might have not oxidized to Ti^{4+} as is indicated by the thermogravimetry.

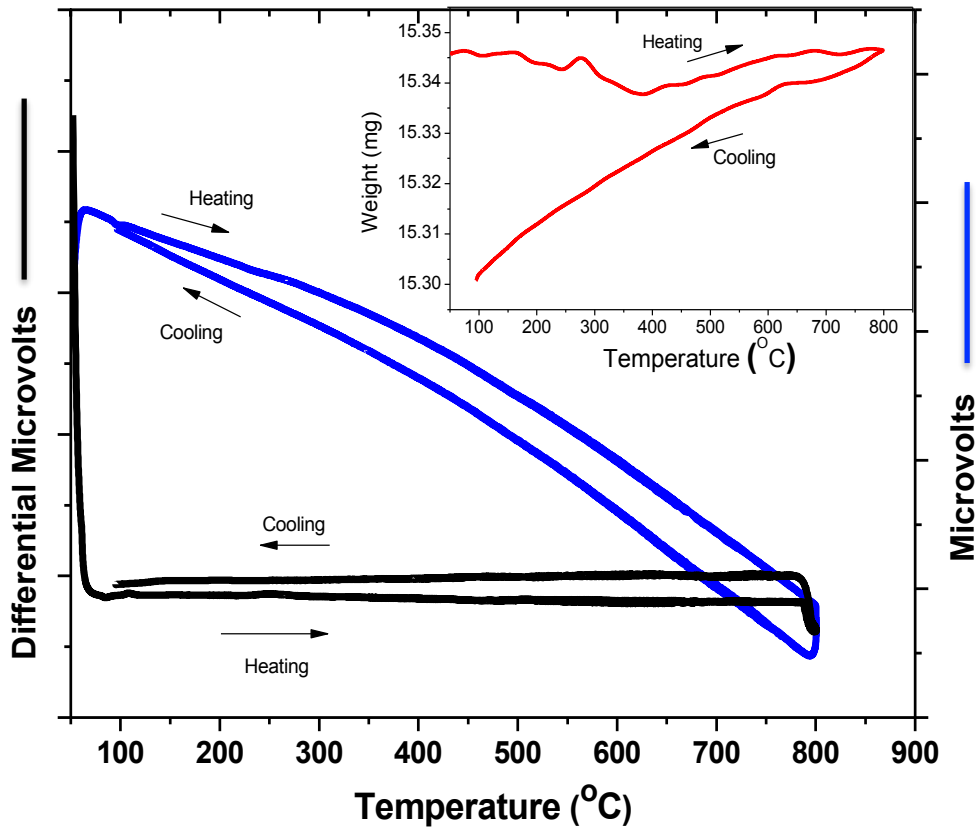


Figure 5.2 (d): DTA, TGA and differential DTA for the sample $x = 0.20$.

5.1.3 Coefficient of thermal expansion (CTE)

The dilatometry utilizes either transformation strains or thermal strains generating the basic data in the form of curves of dimension against time and temperature. The coefficient of linear expansion, also known as expansivity. It is the ratio of the change in length per °C to the length at 0 °C (dL/L_0). CTE is attributed to the asymmetric potential well in the systems [26]. Generally, deep potential wells are more symmetrical about the equilibrium position in comparison to shallow potential wells. Thermal expansion for a given substance tends to be small for strongly bonded materials in comparison to weakly bonded materials. The plots between expansivity and differential of expansivity with respect to temperature are shown in fig.5.3(a-d).

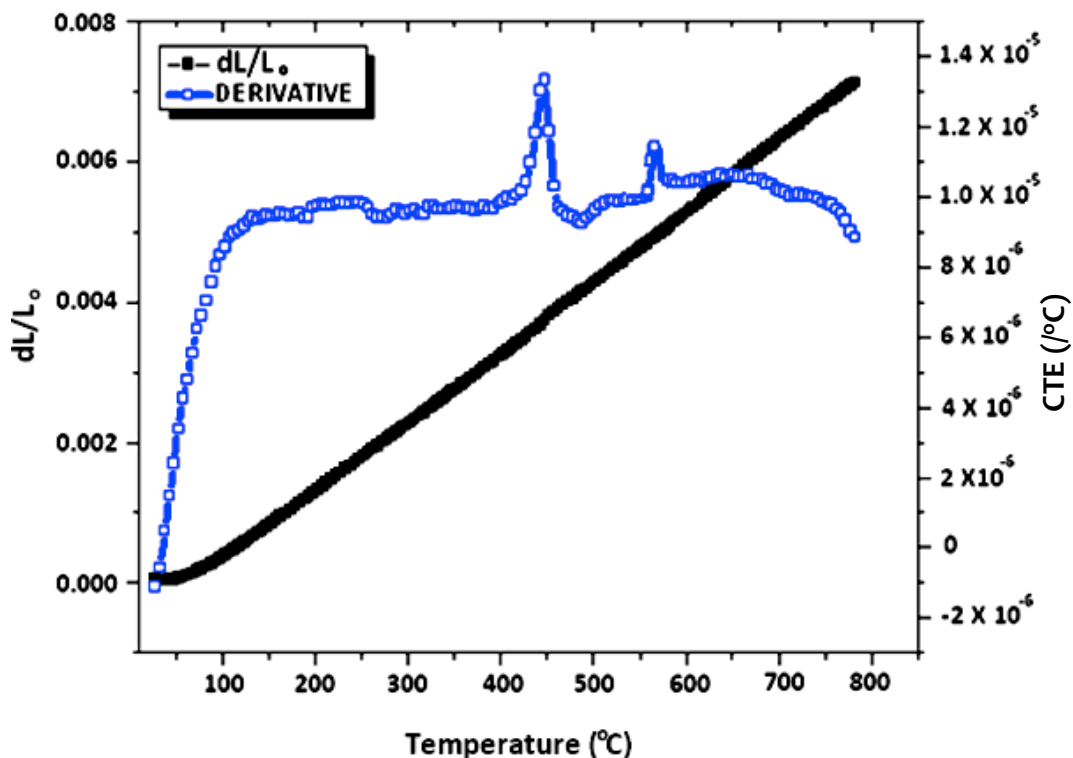


Figure 5.3 (a): Expansivity (dL/L_0) and its derivative curves (CTE) for the sample $x = 0.05$.

The technical thermal expansion coefficient has been calculated from the slope of expansivity vs. temperature curve. The physical thermal expansion coefficient values have been calculated from the differential of expansivity curve. The physical CTE gives point value reaction i.e. the CTE can be evaluated at any temperature whereas technical CTE gives the CTE within a defined temperature range. The CTE of all the samples at different temperature regions are listed in table 5.2.

Table 5.2: CTE of all the samples.

Sample name	Technical CTE from RT-800 °C (/°C)	Technical CTE from 600-800 °C (/°C)	Physical value of CTE at 800 °C (/°C)
$\text{Bi}_2\text{V}_{0.95}\text{Ti}_{0.05}\text{O}_{5.5-\delta}$	9.56×10^{-6}	9.73×10^{-6}	8.82×10^{-6}
$\text{Bi}_2\text{V}_{0.90}\text{Ti}_{0.10}\text{O}_{5.5-\delta}$	10.12×10^{-6}	9.82×10^{-6}	9.36×10^{-6}
$\text{Bi}_2\text{V}_{0.85}\text{Ti}_{0.15}\text{O}_{5.5-\delta}$	9.93×10^{-6}	9.89×10^{-6}	10.06×10^{-6}
$\text{Bi}_2\text{V}_{0.80}\text{Ti}_{0.20}\text{O}_{5.5-\delta}$	10.04×10^{-6}	9.91×10^{-6}	10.25×10^{-6}

The $\text{Bi}_2\text{V}_{0.80}\text{Ti}_{0.20}\text{O}_{5.5-\delta}$ oxide at 800 °C exhibited higher CTE value than all other samples in present investigation indicating higher disorder/weak bonding in it. This means CTE value increased when the prepared oxide undergoes maximum structural rearrangement during

maximum disorder. From fig. 5.3(a), it is clear that two peaks appear at 422 °C and 552 °C for $x = 0.05$, which corresponds to the phase transitions.

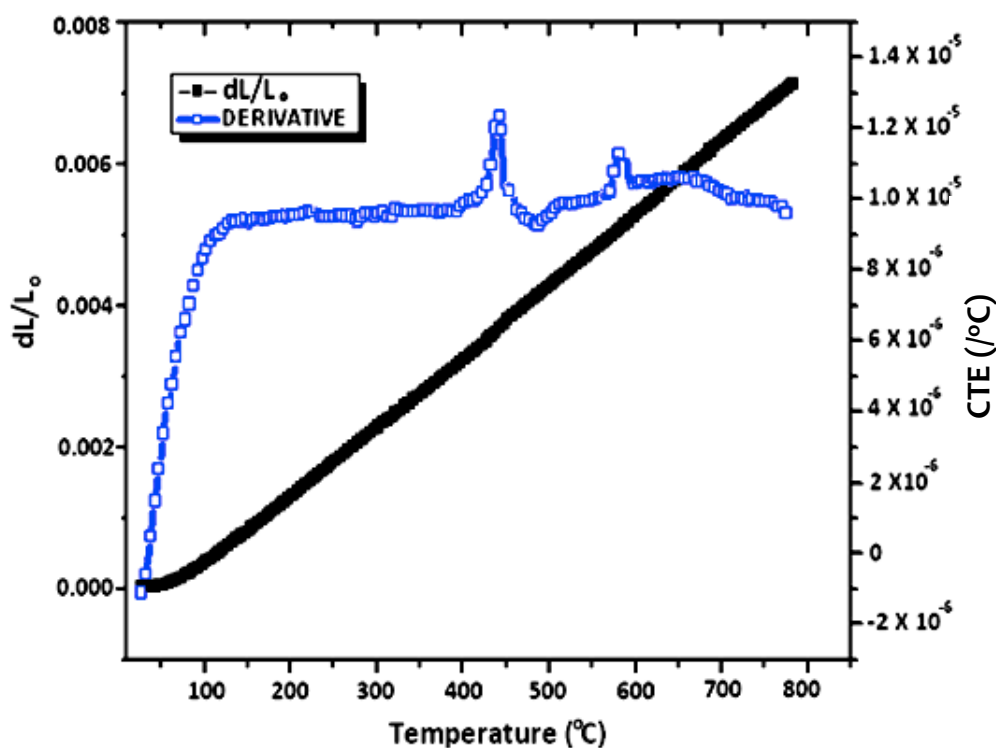


Figure 5.3(b): Expansivity and its derivative curves for the sample $x = 0.1$.

Similarly, peaks at 416 °C and 537 °C have been obtained for $x = 0.10$ (fig. 3(b)). Only one peak appears at 304 °C for $x = 0.15$ which could be due to some structural rearrangement. No peak appeared for $x = 0.20$ indicating the absence of any phase transition. The physical CTE corresponding to the phase transitions have been listed in table 5.3.

Table 5.3: CTE during phase transitions.

Sample name	α/β	β/γ
$\text{Bi}_2\text{V}_{0.95}\text{Ti}_{0.05}\text{O}_{5.5-\delta}$	13.8×10^{-6}	11.9×10^{-6}
$\text{Bi}_2\text{V}_{0.90}\text{Ti}_{0.10}\text{O}_{5.5-\delta}$	12.2×10^{-6}	11.2×10^{-6}
$\text{Bi}_2\text{V}_{0.85}\text{Ti}_{0.15}\text{O}_{5.5-\delta}$	10.4×10^{-6} at 302 °C	
$\text{Bi}_2\text{V}_{0.80}\text{Ti}_{0.20}\text{O}_{5.5-\delta}$	NO TRANSITION	

α/β transition is having high CTE as compared to β/γ transition for both $x = 0.05$ and 0.10. The obtained results clearly indicated that the phase transition (α/β) region is more asymmetric and unstable than (β/γ) region. Whereas, no such transitions have been observed for $x = 0.15$ and

0.20. The results and various transitions obtained are in correlation with the thermal analysis results.

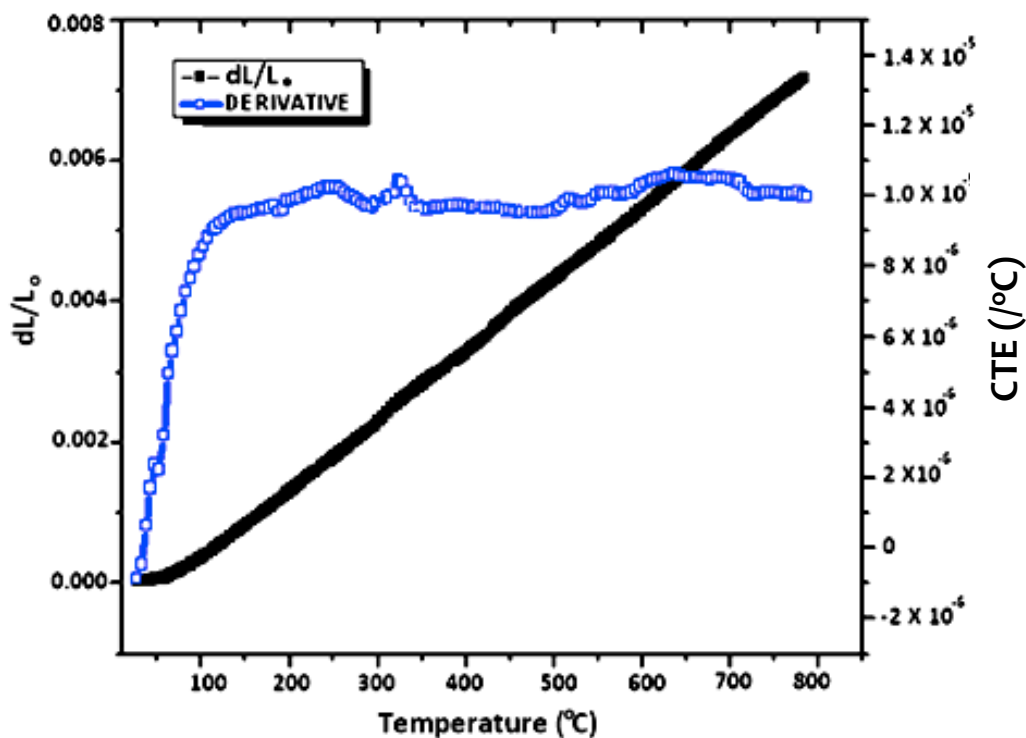


Figure 5.3(c): Expansivity and its derivative curves for the sample $x = 0.15$.

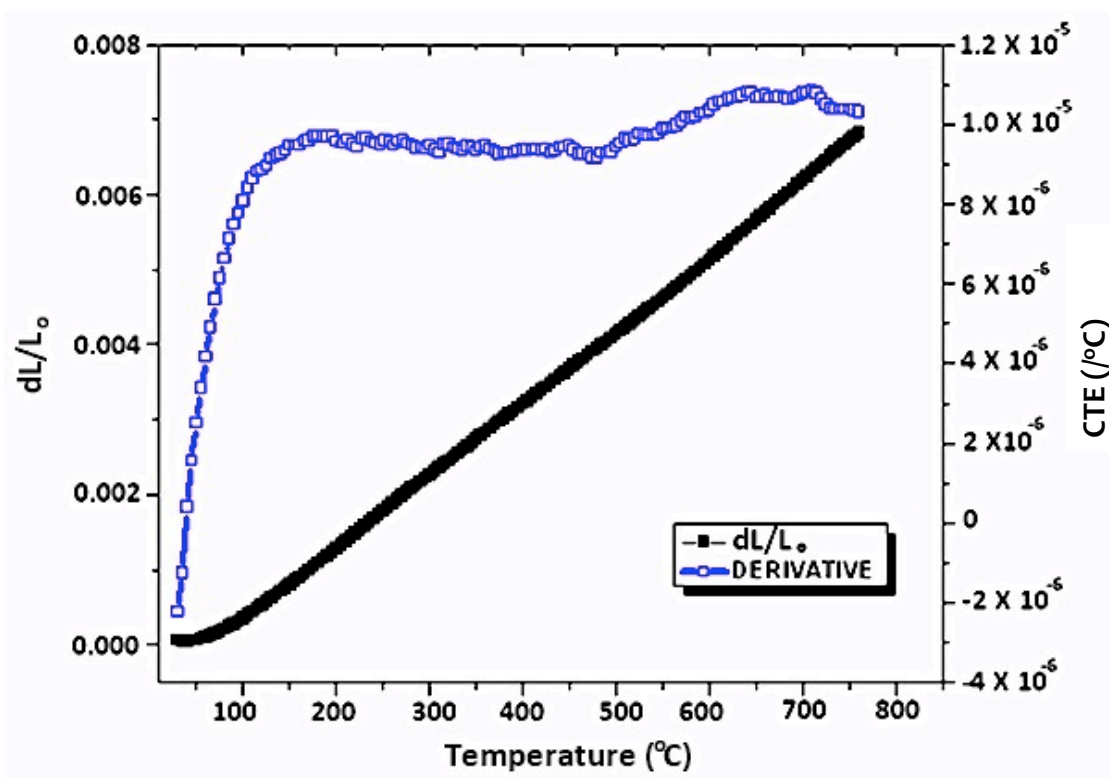


Figure 5.3(d): Expansivity and its derivative curves for the sample $x = 0.20$.

5.1.4 Conductivity analysis

The electrical conductivity results in the form of Arrhenius plots and are shown in fig. 5.4 for $\text{Bi}_2\text{V}_{1-x}\text{Ti}_x\text{O}_{5.5-\delta}$ ($0.05 \leq x \leq 0.20$). The figure clearly manifests the transition temperatures for all dopings i.e. $0.05 \leq x \leq 0.20$. For $x = 0.05$ and 0.10 , the Arrhenius plots of conductivity clearly shows three transition regions attributed to three principle polymorphs of $\text{Bi}_2\text{VO}_{5.5-\delta}$. For $x = 0.05$, the sample exhibits pronounced conductivity jump near 442°C and 541°C which are related to (β/α) and (γ/β) transitions as also observed in CTE and DTA measurements. Similar transitions have been observed for $x = 0.10$ at 386°C and 488°C , respectively. For $x = 0.15$, the conductivity jump for (β/α) have almost disappeared along with a small change in slope. However, continuous jump from low conducting to high conducting state is observed at 630°C which could be due to some structural relaxation. Doping with $x = 0.20$ leads to disappearance of (β/α) and (γ/β) .

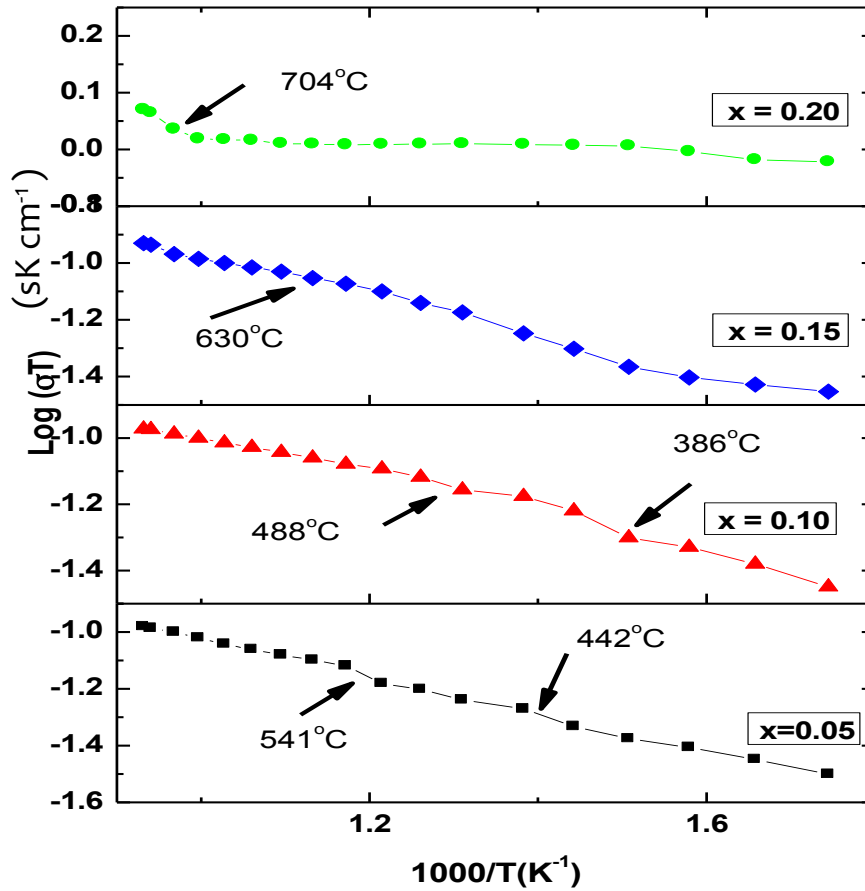


Figure 5.4: Arrhenius plots for $\text{Bi}_2\text{V}_{1-x}\text{Ti}_x\text{O}_{5.5-\delta}$ ($0.05 \leq x \leq 0.20$) indicating phase transitions during cooling cycles.

Only a small inflection at 704 °C is observed which could be related to oxygen relaxation during phase change from γ' to γ [27-28]. Hence small difference in atomic arrangement can notably change the transition behavior. The results obtained from DTA and dilatometry is in well agreement with conductivity results. The conductivity was calculated using the formula:

$$\sigma = l/RA \quad (5.2)$$

where l is the thickness of the pellet, A is the area of cross-section of gold sputtered pellet and R is the total resistance of sample calculated from the point of intersection of Cole-Cole semicircle plot on the real axis. The electrical conductivities at different temperatures as well as activation energies are listed in table 5.4. Activation energy can be obtained from the slope of Arrhenius plot. Break in Arrhenius plots also signify the corresponding change in activation energy for conduction.

Table 5.4: Conductivity and activation energy for samples.

Sample name	σ_{400} (S cm ⁻¹)	σ_{600} (S cm ⁻¹)	σ_{800} (S cm ⁻¹)	$E_a < 400^\circ\text{C}$ (in eV)	$E_a > 500^\circ\text{C}$ (in eV)	Density (gm/cm ³)
Bi ₂ V _{0.95} Ti _{0.05} O _{5.5-δ}	6.71×10^{-5}	9.01×10^{-5}	9.74×10^{-5}	0.29	0.22	7.42
Bi ₂ V _{0.90} Ti _{0.10} O _{5.5-δ}	7.71×10^{-5}	9.11×10^{-5}	9.67×10^{-5}	0.27	0.20	7.38
Bi ₂ V _{0.85} Ti _{0.15} O _{5.5-δ}	8.71×10^{-5}	1.11×10^{-4}	1.78×10^{-4}	0.31	0.24	7.29
Bi ₂ V _{0.80} Ti _{0.20} O _{5.5-δ}	1.71×10^{-4}	1.08×10^{-3}	1.17×10^{-3}	0.25	0.19	7.31

From table 5.4, it is clear that activation energy of conduction is higher for low temperatures. The change in activation energy is also associated with association-dissociation of defect clusters [28-29]. The sample $x = 0.20$ exhibits highest conductivity of 1.17×10^{-3} S cm⁻¹ at 800 °C which indicates that both the vacancy concentration and pathways for O²⁻ motion are optimized in this sample. The conductivity of $x = 0.20$ at 800 °C higher than that of $x = 0.05$ by two orders of magnitude. Similar trend of conductivity has been observed at 600 °C. In addition to this, the conductivity of $x = 0.20$ changes only by an order of magnitude from $x = 0.05$ at 400 °C. This can be attributed to small thermal energy at low temperatures to promote the migration of oxygen. Above 400 °C, the conductivity rises due to thermal activation. The sample $x = 0.20$ shows two order higher conductivity. It may be ascribed to good density than earlier reported density. In summary, it indicates that the processing conditions play very important role to decide the transport properties. Fig. 5.5 shows the variation of imaginary part of impedance Z'' with frequency for all samples at 600 °C. With the increase of frequency and doping concentration, the magnitude of Z'' decreases which is consistent with the results obtained from

Arrhenius plots. The calculated densities have been listed in table 5.4. All the synthesized samples have been obtained with density between 93-95%, which is in good agreement with literature [30].

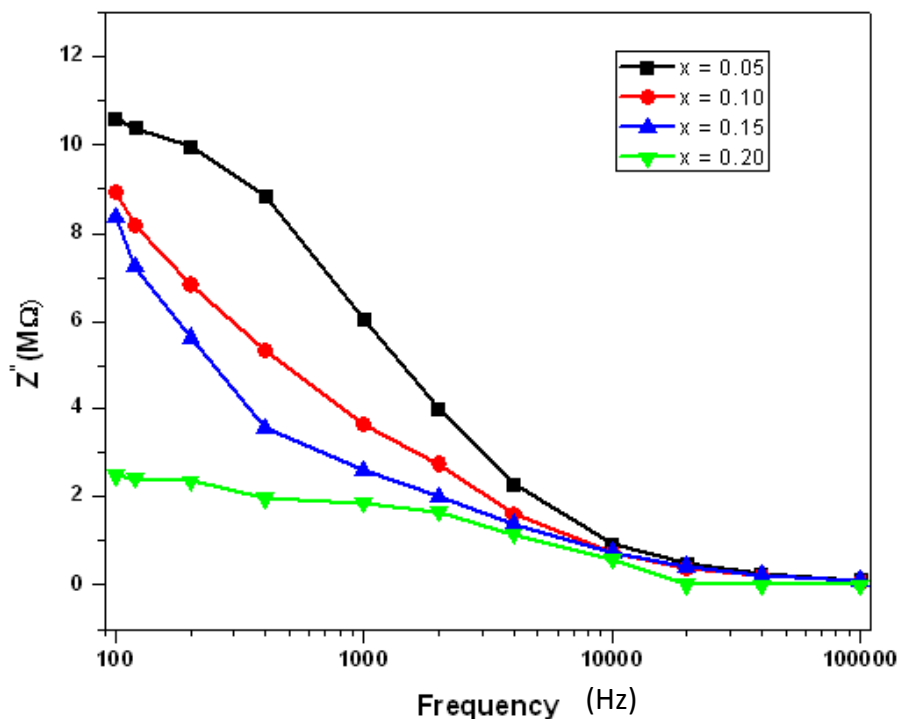


Figure 5.5: Plot of frequency with imaginary part of impedance for $\text{Bi}_2\text{V}_{1-x}\text{Ti}_x\text{O}_{5.5-\delta}$ ($0.05 \leq x \leq 0.20$) at 600 °C.

5.1.5 Analysis of microstructure and grain size

The fractured surface of $\text{Bi}_2\text{V}_{1-x}\text{Ti}_x\text{O}_{5.5-\delta}$ ($0.05 \leq x \leq 0.20$) have been analyzed by SEM and shown in figs. 5.6(a-d), respectively. The porosity as well as grain size increased with dopant concentration. The microstructures for $x \leq 0.1$ (fig. 5.6(a-b)) exhibited cluster like non-uniform pattern with subsequently decreased porosity which are in well agreement with the results obtained for density. However, the particles are well connected to each other having porous network. From fig. 5.6(d), it is clearly depicted that the most homogenous microstructure is observed for $\text{Bi}_2\text{V}_{0.80}\text{Ti}_{0.20}\text{O}_{5.5-\delta}$. The grains are found to be more uniform with observable porosity for this sample. No segregation of elements in the bulk materials is observed except for $x = 0.25$. As the dopant concentration increased from $x = 0.05$ to $x = 0.20$, the grain size subsequently increased for all the samples. The grain size, standard deviation with variance upto ± 0.001 are listed in table 5.5.

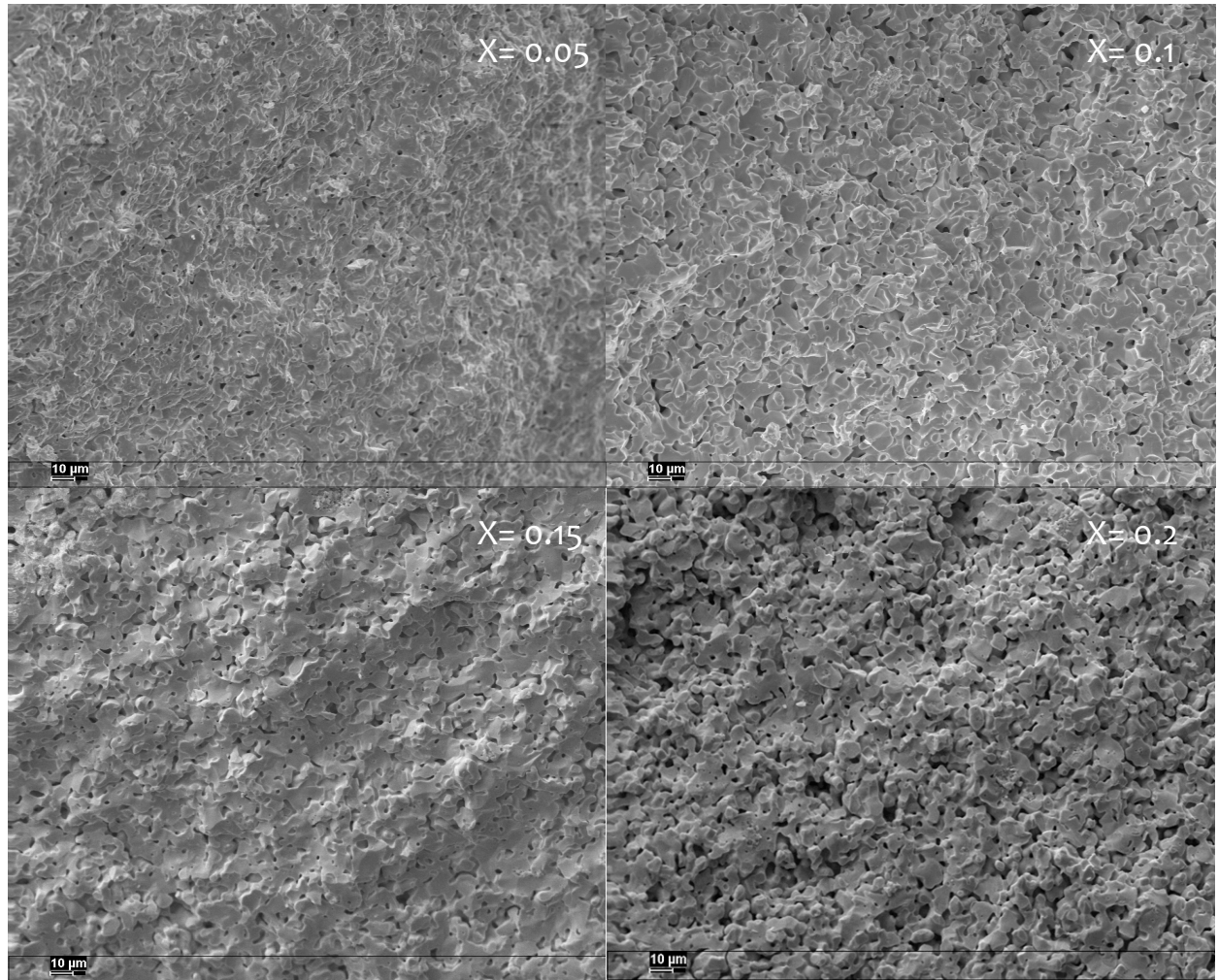


Figure 5.6: Microstructure for for $\text{Bi}_2\text{V}_{1-x}\text{Ti}_x\text{O}_{5.5-\delta}$ ($0.05 \leq x \leq 0.20$) doped sample.

Standard deviation gives variation or dispersion from the average value. The sampling of 50 grains is done to obtain the average grain size and subsequently standard deviation. Low standard deviation for $\text{Bi}_2\text{V}_{0.85}\text{Ti}_{0.15}\text{O}_{5.5-\delta}$ indicates that the data points tend to be very close to the mean and clustered around it. High standard deviation for $\text{Bi}_2\text{V}_{0.90}\text{Ti}_{0.10}\text{O}_{5.5-\delta}$ indicates that the data are spread out over a large range of values.

Table 5.5: Grain size, standard deviation (σ) and variance (σ^2) for all the samples.

Sample name	Average grain size (μm)	Standard deviation (σ)	Variance (σ^2)
$\text{Bi}_2\text{V}_{0.95}\text{Ti}_{0.05}\text{O}_{5.5-\delta}$	3.31	1.56	2.44
$\text{Bi}_2\text{V}_{0.90}\text{Ti}_{0.10}\text{O}_{5.5-\delta}$	3.90	1.78	3.17
$\text{Bi}_2\text{V}_{0.85}\text{Ti}_{0.15}\text{O}_{5.5-\delta}$	5.23	1.44	2.07
$\text{Bi}_2\text{V}_{0.80}\text{Ti}_{0.20}\text{O}_{5.5-\delta}$	7.74	1.51	2.28

Grain size is found to be highest for $\text{Bi}_2\text{V}_{0.80}\text{Ti}_{0.20}\text{O}_{5.5-\delta}$ and lowest for $\text{Bi}_2\text{V}_{0.95}\text{Ti}_{0.05}\text{O}_{5.5-\delta}$. The structural stability and homogeneity of these samples is likely to have dominating impact on their conductivity as well as thermal properties.

5.2 $\text{Bi}_2\text{V}_{0.80}\text{Ti}_{0.20}\text{O}_{5.5-\delta}$ oxygen ion conductor

γ phase is stabilized against α and β for $\text{Bi}_2\text{V}_{0.80}\text{Ti}_{0.20}\text{O}_{5.5-\delta}$ at room temperatures, which is evident from XRD as well as thermal analysis results. This sample has shown maximum conductivity of 1.17×10^{-3} S/cm and minimum activation energy of 0.19 eV at 800 °C. The $\text{Bi}_2\text{V}_{0.80}\text{Ti}_{0.20}\text{O}_{5.5-\delta}$ oxide at 800 °C exhibited higher CTE value than all other samples in present investigation indicating higher disorder in it. The sample has shown high density as well as reduction during the cooling cycle indicating that Ti^{3+} might have not oxidized to Ti^{4+} . Hence $\text{Bi}_2\text{V}_{0.80}\text{Ti}_{0.20}\text{O}_{5.5-\delta}$ has been chosen for interaction study with glasses.

5.3 X-ray diffraction (XRD) of coupled glasses

5.3.1 XRD of coupled ML glass with YSZ and TBV

The XRD of coupled glasses for TBV and YSZ electrolyte are shown in figs. 5.7 and 5.8, respectively. The XRD of coupled glasses with YSZ and TBV could not form any crystalline phase even after 100 h heat-treatment. The presence of broad halo is an evidence of amorphous phase for coupled seals heat-treated upto 100 h. Partial crystallization has been observed after 750 h heat-treatment at 800 °C for the coupled seal with TBV as is shown on fig. 5.7 where enstatite (MgSiO_3) [ICDD – 35-0610] and pyrochlore ($\text{La}_2\text{Si}_2\text{O}_7$) [ICDD- 72-2456] phases got precipitated. The formation of these phases can be explained using following mechanism:



During devitrification process, enstatite phase might have formed first followed by pyrochlore phase. It is well reported that pyrochlore phase is highly ordered phase [31]. Titanium present in TBV can act as nucleating agent and has high tendency for the formation of ordered zones. This could be attributed to high field strength of titanium, which is responsible for phase separation and nucleation of crystalline phases [32-33].

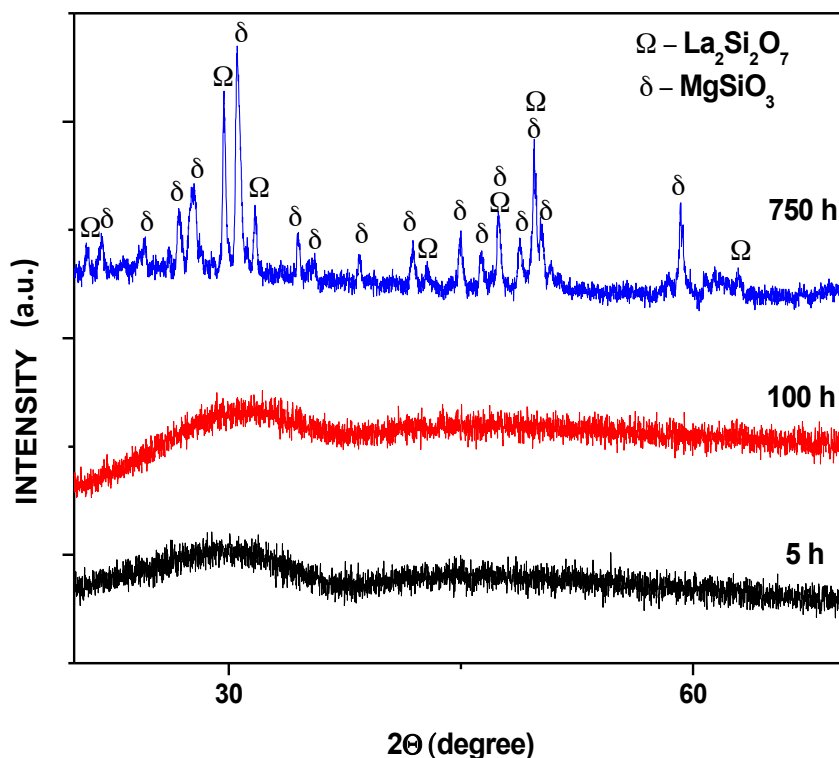
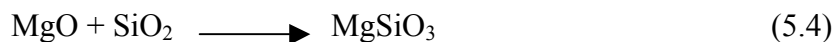


Figure 5.7: XRD of coupled ML glass with intermediate temperature TBV electrolyte.

For coupled ML glass with YSZ, only enstatite phase appeared with complete absence of any pyrochlore phase after prolonged heat-treatment of 750 h at 850 °C. No zirconate phase could be seen in the diffractogram (fig. 5.8). Following mechanism can be proposed during enstatite phase formation:



This could be explained as follows. The diffusion of zirconia must have occurred in glass seal which is in contact with YSZ. In borosilicate glasses, the ZrO_2 solubility is generally associated with change of boron network hence retarding the phase separation [34]. Hence, the diffusion of zirconia might have suppressed the nucleation as well as growth of crystalline phases like pyrochlore ($\text{La}_2\text{Si}_2\text{O}_7$). Moreover, MgSiO_3 phase appearing for coupled glass with YSZ (heat-treated at 850 °C for 750 h) have shown reduced peak intensity in the diffractogram as compared to coupled glass with TBV (heat treated at 800 °C for 750 h). This indicates lower crystallinity in case of coupled glass with YSZ after prolonged heat-treatment of 750 h.

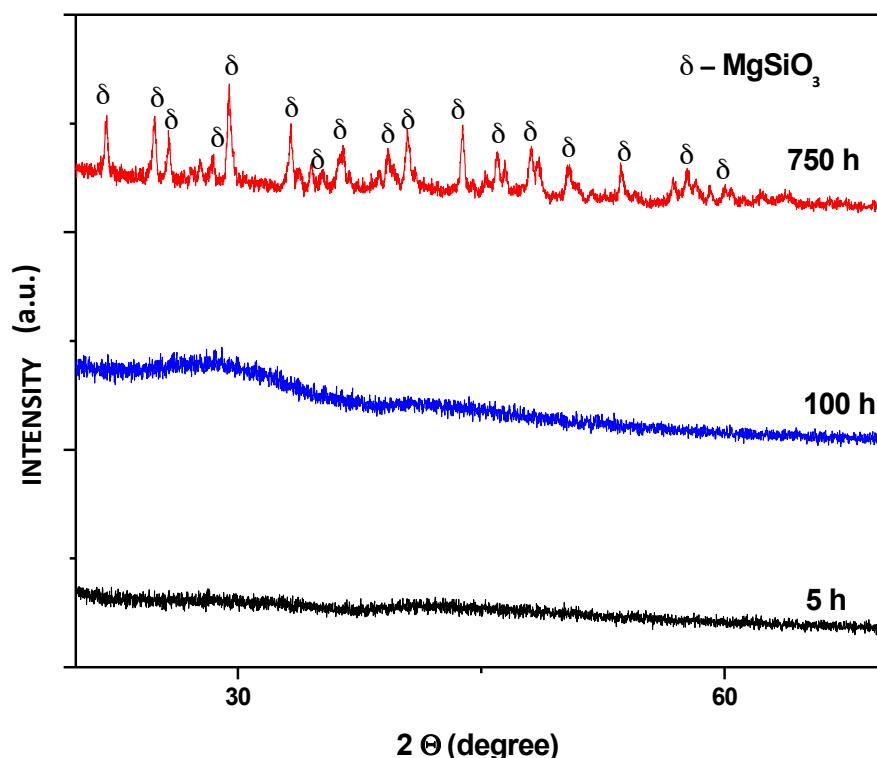


Figure 5.8: XRD of coupled ML glass with high temperature YSZ electrolyte.

ML glass required prolonged duration of heat-treatment to get converted to ML glass-ceramic indicating sluggish crystallization kinetics for this particular glass. This could be due to its higher activation energy and small frequency factor (as discussed in results and discussions-I). Higher temperature and longer time required for a glass to devitrify means high devitrification resistance of that glass [35-36, 37]. In addition to this, MgO has been used as network modifier in present glass, which is also crystallization inhibitor [38].

5.3.2 XRD of coupled CL glass with YSZ and TBV

Fig. 5.9 and 5.10 shows the XRD of coupled CL glass with TBV and YSZ, respectively. For coupled CL glass with TBV, the glass did not convert to glass-ceramic after heat-treatment of 5 h at 800°C , which is clear from XRD diffractogram (fig. 5.9). After heat-treatment of 100 h at 800°C , Ca_2SiO_4 (ICDD- 03-0776) phase has formed. The prolonged heat-treatment of 750 h at 800°C has resulted in increase in volume fraction of Ca_2SiO_4 (calcium orthosilicate) without the emergence of any other phase.

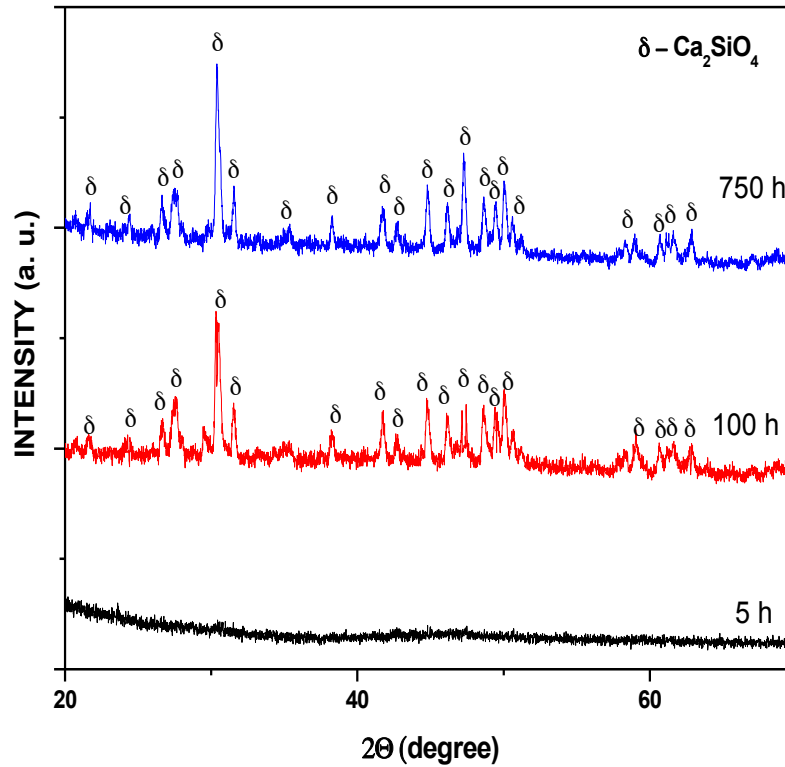
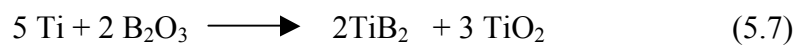
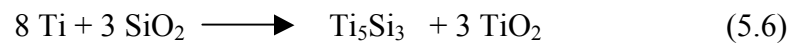


Figure 5.9: XRD of coupled CL glass with intermediate temperature TBV electrolyte.

The chemical reaction mechanism can be proposed as follows:

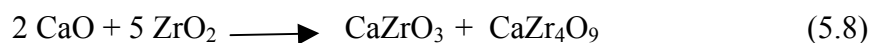


No titanium or vanadium rich phase has been observed in the XRD diffractograms though their diffusion is on the higher side as compared to other elements present in CL and bismuth vanadate (discussed later). Titanium rich phases are harmful for the functioning of SOFC [39-40]. Due to higher chemical reactivity of titanium, dense and self-healing adherent oxide is formed by it. The free energy of titania is low ($\Delta G = -677.8 \text{ kJ/mol}$ at 1000°C) [41]. Generally titanium reacts with borosilicate glasses, which can lead to following reactions [42-43]:

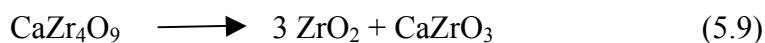


Interfacial silicide phase (Ti_5Si_3) is more brittle than interfacial boride phase (TiB_2). Moreover, silicide phase bonds less stronger than the boride phase. XRD of coupled glass with titania

doped bismuth vanadate (TBV) completely precludes the presence of any boride or silicide phase. For coupled CL glass with YSZ, the pattern exhibits amorphous halo after heat – treatment of 5 h at 850 °C as shown in fig. 5.10. But after 100 h treatment at 850 °C, peaks of CaZrO_3 have appeared in the diffractogram. Further heat-treatment of sample for 750 h at 850 °C results in the emergence of new CaZr_4O_9 phase along with CaZrO_3 (calcium zirconate). The CaZrO_3 structure must have formed through initial diffusion from glass and subsequent reaction of Ca^{2+} with YSZ substrate. The following reaction kinetics might be given:



CaZr_4O_9 is a stable phase at high temperatures and dissociates into two crystalline phases at 921 °C i.e. monoclinic ZrO_2 and CaZrO_3 [44] as follows:



The formation of crystalline silicate or pyrochlore phase is not observed. Moreover, in all diffusion couples, cristobalite phase has not formed.

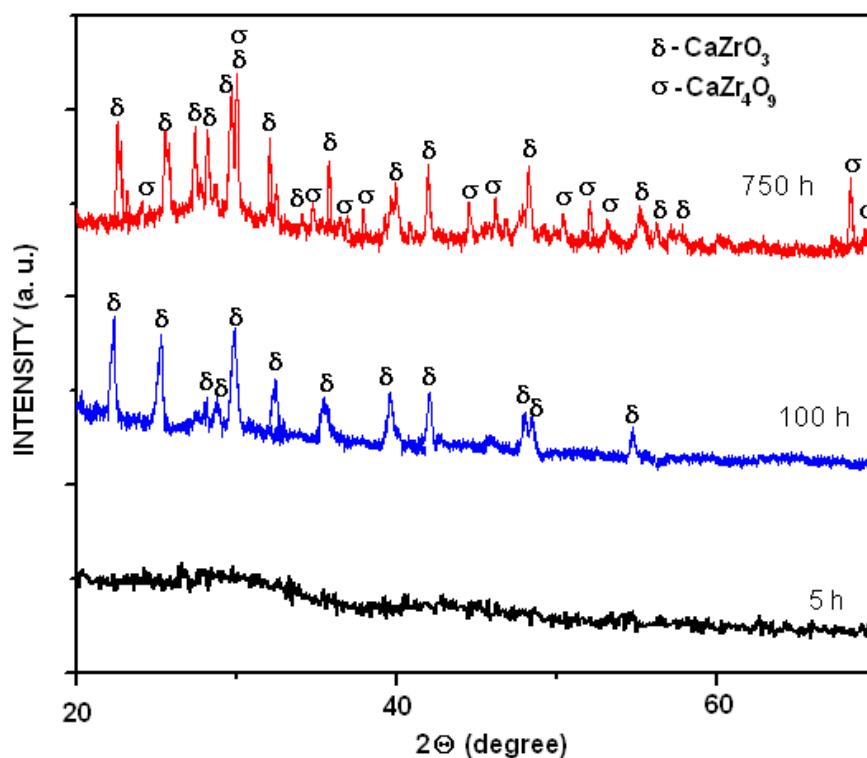


Figure 5.10: XRD of coupled CL glass with high temperature YSZ electrolyte.

The cristobalite phase creates thermal stress due to its displacive transformation upon cooling leading to decrease in volume [38]. Conclusively, zirconia and titanium has diffused out to marked extent (discussed later), but still no detrimental phases have been obtained. Zirconia is generally stable with higher coordination numbers and can act as network modifier in glass network, whereas titanium can be tetrahedrally coordinated and can act as network former in glass network [45].

5.3.3 XRD of coupled SL glass with YSZ and TBV

The XRD analysis has revealed the devitrification and specific type of devitrified phases as a function of thermal treatment time. Glass network connectivity and homogeneity exhibit influence on devitrification resistance of the glass system. If the glass posses higher inhomogeneity in its structural units, then the devitrification increases. Fig. 5.11 and 5.12 shows the XRD of coupled SL glass with TBV and YSZ, respectively.

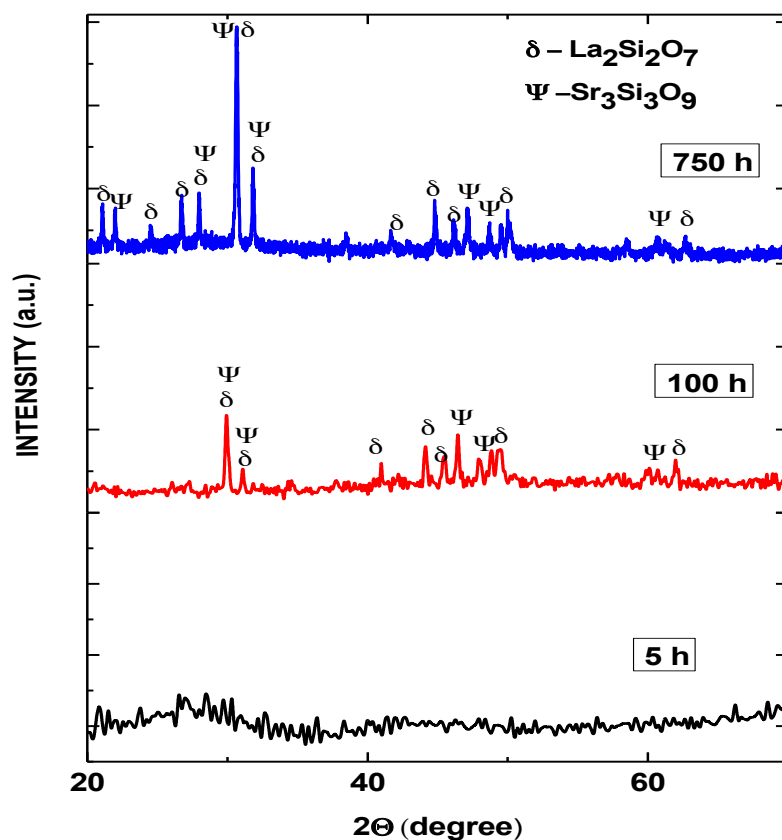
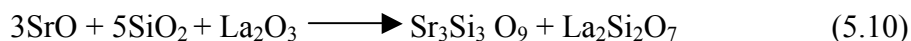


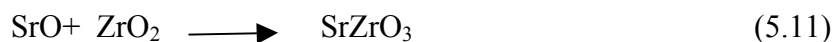
Figure 5.11: XRD of coupled SL glass with intermediate temperature TBV electrolyte.

Coupled SL glass with TBV remained amorphous after heat-treatment of 5 h at 800 °C, which is clear from diffractogram (fig. 5.11). Hence the glass has not shown any sign of devitrification and demonstrated itself as a very stable seal. After heat-treatment of 100 h at 800 °C, $\text{Sr}_3\text{Si}_3\text{O}_9$ and $\text{La}_2\text{Si}_2\text{O}_7$ phase has formed. The devitrified peaks become stronger with thermal treatment time of 750 h at 800 °C. After 750 h treatment, the diffraction peaks are quite stronger than those of 100 h treated coupled glass sample. This clearly implies that devitrification must have occurred extensively during this thermal treatment period. The reaction mechanism can be given as follows:



La^{3+} and Sr^{2+} cations always have higher tendency to bond with glass forming cations via NBO atoms [46-47]. The complex interaction between glass structural silica unit and modifiers leads to devitrification and Sr-La containing crystalline phase formation. La-O-Si containing cations also act as nucleation sites [48]. Lanthanum silicate is extremely refractory in nature with a melting point of 1750 °C [49]. It contributes to overall performance of glass ceramics in terms of high temperature stability. Generally, TiO_2 is soluble in silicate melts but during subsequent cooling or heating, large numbers of submicroscopic particles are precipitated which assist the development of major crystalline phases. Nucleating process becomes fast which results in high nucleation density and transparent glass-ceramic [34].

Coupled SL glass with YSZ is still amorphous with no devitrified phase as demonstrated by broad XRD pattern after heat-treatment of 5 h at 850 °C (fig. 5.12). No crystallization or phase separation has been observed after 5 h treatment. Small devitrification peaks of SrZrO_3 have appeared in the diffractogram after 100 h treatment at 850 °C. Further heat-treatment of 750 h at 850 °C results an increase in volume fraction of this phase. The following reaction kinetics must have been followed:



Zirconia has diffused to a considerable extent on the glass side and could have entered the network former position. Furthermore, the interaction between modifier and former has lead to the formation of zirconate phase. Though vanadium and titanium has substantially diffused out of electrolyte towards the glass side (discussed later), still no phase has been detected which involves their presence. Hence, the formation of detrimental phases is completely precluded in the present case.

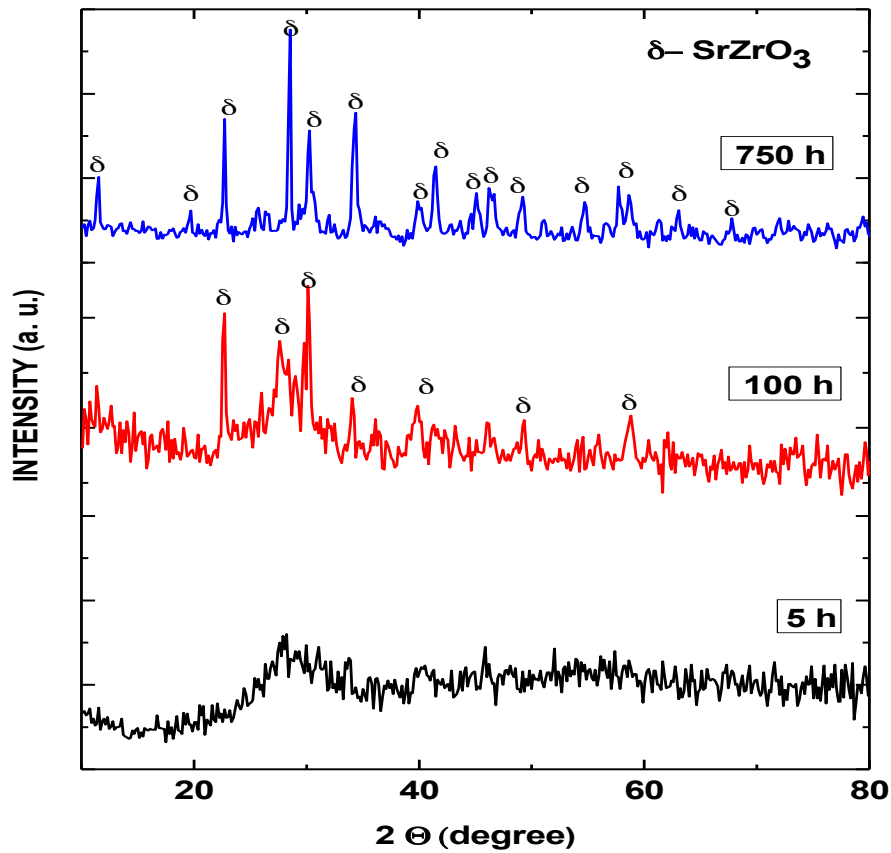


Figure 5.12: XRD of coupled SL glass with high temperature YSZ electrolyte.

Moreover, with increasing time duration of heat-treatment, the relative intensity of formed phases increases indicating decrease in residual glass fraction. Initial stages of devitrification are governed by thermodynamics which mainly involves phase separation and nucleation. Generally, nucleation initiates from defect sites. During later stages of devitrification, the kinetic aspect dominates which includes areal density effects, crystallite size and growth direction. Nucleation is further followed by growth process. In glasses, after some critical period of time, further growth on surface is limited due to phenomena of growing crystal impingement [50]. Crystal growth stops and only those crystallites whose fastest growing direction is perpendicularly oriented to glass surface keeps on growing. The time from lateral growth to perpendicular direction is given by [51]:

$$T = 1/2\mu\sqrt{v} \quad (5.12)$$

μ is the crystal glass moving velocity and v is number of nucleation sites. As the obtained frequency is quite high as described in previous section, hence the time for growth is small. In this respect, the density of nucleation site directly affects crystallization process.

5.3.4 XRD of coupled BL glass with YSZ and TBV

Fig. 5.13 and 5.14 shows the XRD of coupled BL glass with TBV and YSZ, respectively to understand the nucleation kinetics of different crystalline phases. For coupled BL glass with TBV and YSZ, no crystalline phase formation could be seen even after 100 h treatment.

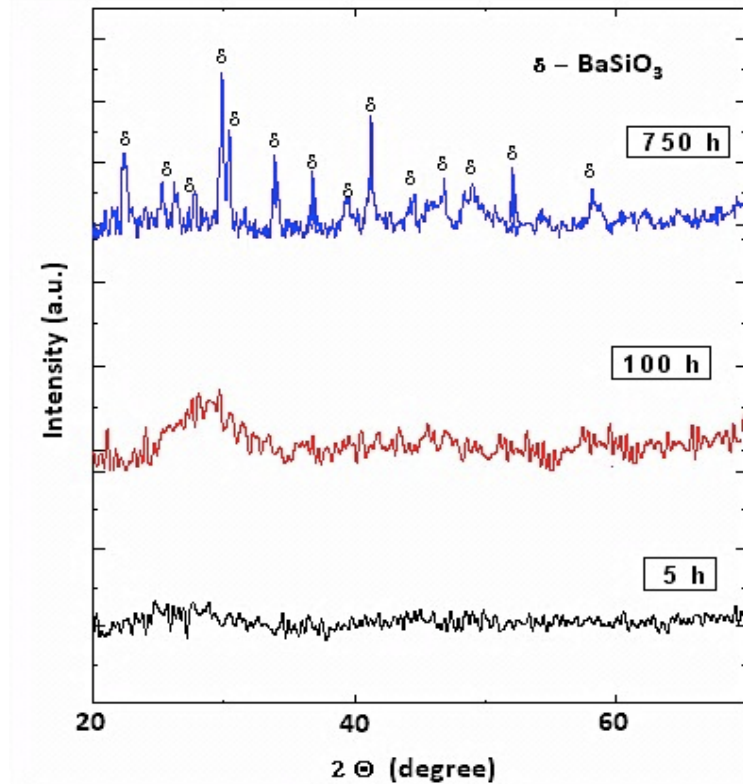


Figure 5.13: XRD of coupled BL glass with intermediate temperature TBV electrolyte.

After 750 h treatment, BL glass gets converted to glass-ceramic as BaSiO_3 phase has been obtained for both the coupled glasses. These glass ceramics are basically polycrystalline solids with residual glassy matrix, which leads to their characteristic microstructure and hence better performance [52]. Moreover, higher temperature and longer time is required for BL glass indicating its high devitrification resistance. La_2O_3 is considered to be an oxide, which is used to reduce the tendency of glass melt to devitrify. It also retards the crystallization if added upto 3-10%, and therefore improves the sintering and flow characteristics for precursor glass powders during thermal processing [49]. The reaction kinetics must have followed the following reaction in both the cases:



Generally, barium silicate phases have high CTE. For coupled TBV/BL glass, the volume fraction of crystalline phase is more in comparison to coupled YSZ/BL glass. Coupled BL glass

shows low rate of controlled crystallization as is evident from fig. 5.13 and 5.14. The remaining glassy phase in GC acts as major factor for deciding the flow behavior of the GC seal and plays a crucial role in determining the reaction kinetics during chemical interaction between glass seal and SOFC components. Also, such a high amount of glassy phase present in the GC's is expected to exhibit self-healing behavior during SOFC operation [53].

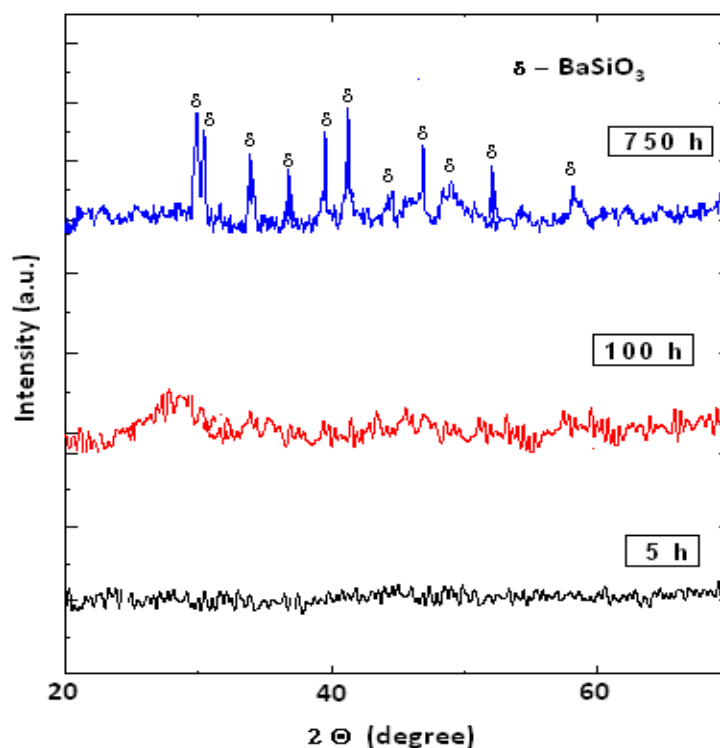


Figure 5.14: XRD of coupled BL glass with high temperature YSZ electrolyte.

During cell operation, sealing materials should not have very fast crystallization otherwise thermal stresses increases, which degrade the efficiency of SOFC [34]. Generally, there are two types of processes by which a phase can transform into another: (a) changes that are initially small in degree but large in spatial extent. During the earlier stages of transformation, these phases resemble the growth of compositional waves. This phase transformation is called spinodal decomposition. Some changes are large in degree, but small in spatial extent. This transformation is termed as nucleation and growth [34]. For the present BL glass, second case is observed. Nucleation of crystalline phases can be controlled in two ways: sometimes the nucleating agents provide the site for nucleation. Secondly, a heat-treatment is designed to provide the appropriate number of nuclei. The temperature should be relatively low in order to

maximize the rate of nucleation. However, the overall rate of crystallization depends on the rate of the crystal growth once nucleation occurs, higher temperatures are required to maximize the growth rate. The low temperature step provides nucleation sites, and the high step speeds the rate of growth of the crystals. The crystallization temperature is 775 °C for BL glass, but the heat-treatment is given at 800 °C and 850 °C, which speed up crystal growth.

5.4 Sealing and microstructural analysis of glasses with intermediate temperature TBV

The present electrolytes/glass seal interfacial studies have been conducted in oxidizing atmosphere. Diffusion must occur prior to chemical reaction. Therefore, diffusion process is the controlling factor for any chemical reaction to occur at the interface. In the present section, the diffusion couple of all glasses with high temperature electrolyte (YSZ) and intermediate temperature electrolyte (TBV) as a function of heat-treatment durations of 5, 100 and 750 h have been investigated to check their interfacial stability. SEM has been done in order to investigate microstructural changes and chemical reactivity at the interface with respect to heat-treatment duration. The diffusion couples have been studied at 850 °C for YSZ and also 800 °C for TBV, respectively. Difference between CTE (α) for TBV and glasses with respect to temperature has been shown in fig. 5.15 (a-d).

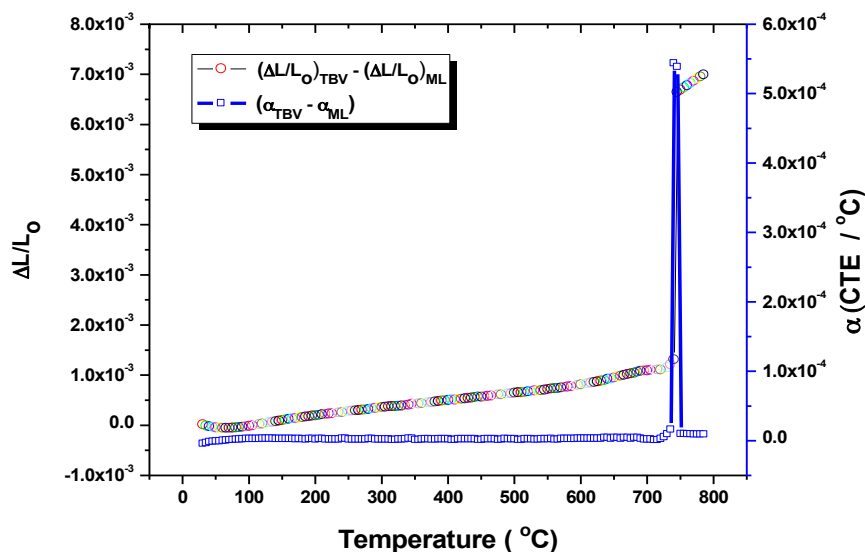


Figure 5.15 (a): Difference between coefficient of thermal expansion (α) for TBV and ML glass with respect to temperature.

From fig. 5.15(a), it is observed that the maximum CTE mismatch for ML/TBV occurs at 741 °C. However, for CL glass (fig. 5.15(b)), maximum CTE mismatch occurs at 756 °C followed

by CTE mismatch at 748 °C. After 756 °C, the stress has become compressive in nature as $CTE_{\text{glass}} > CTE_{\text{TBV}}$ [54]. Fig. 5.15 (c) illustrates that 731 °C seems to be the temperature of maximum stress for SL glass. At the same time, temperature of maximum stress occurs at 712 °C followed by 722 °C for BL glass (fig. 5.15 (d)). For BL glass, compressive stress has dominated at the temperature of maximum stress. The compressive stress generally leads to delamination at the interface. Anyhow, for all these glasses, stress has arisen above T_g and can be tolerated due to viscous flow of the glass [55]. In glass transition region, the properties of glasses are time-dependent. The origin of thermal stress is the restraint to dimensional expansion or contraction. There is always temperature gradient from core to surface of component, which can also induce residual stresses [26]. The heat conduction from inside of glass to surface is slow as it is poor thermal conductor. Sometimes the interior temperature of glass is above T_g , which makes it capable to flow like a viscous material. This viscous flow is also responsible for the contraction at surface. When the inside of glass gets cooled down, then contraction is resisted by rigid outer layers. This further leads to development of compressive stresses inside glass and tensile stresses on the surface of glass. These stresses make glass more prone to cracks or fracture as compared to crystalline ceramic materials.

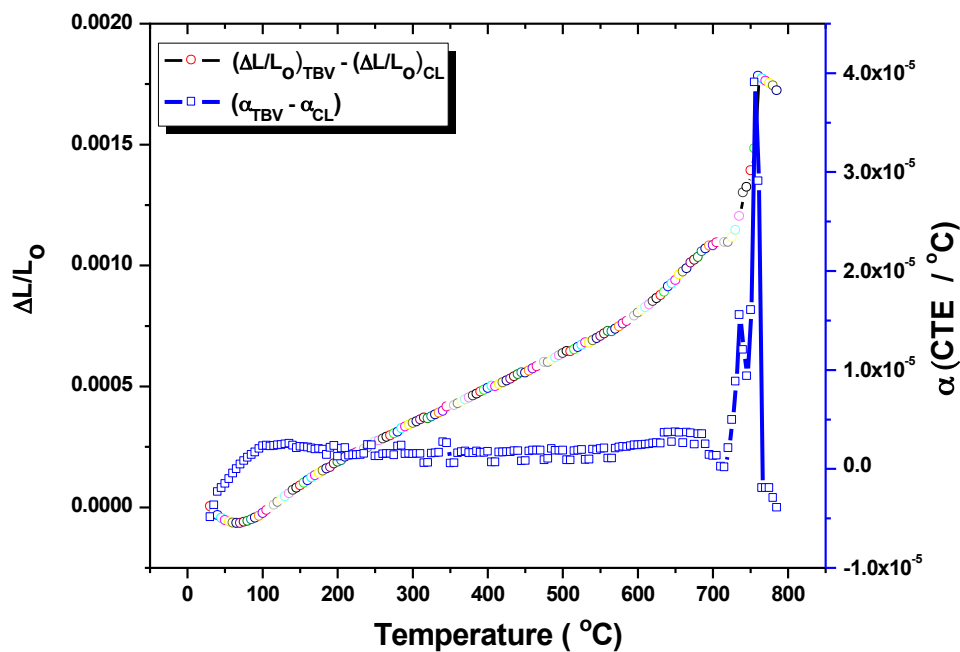


Figure 5.15 (b): Difference between coefficient of thermal expansion (α) for TBV and CL glass with respect to temperature.

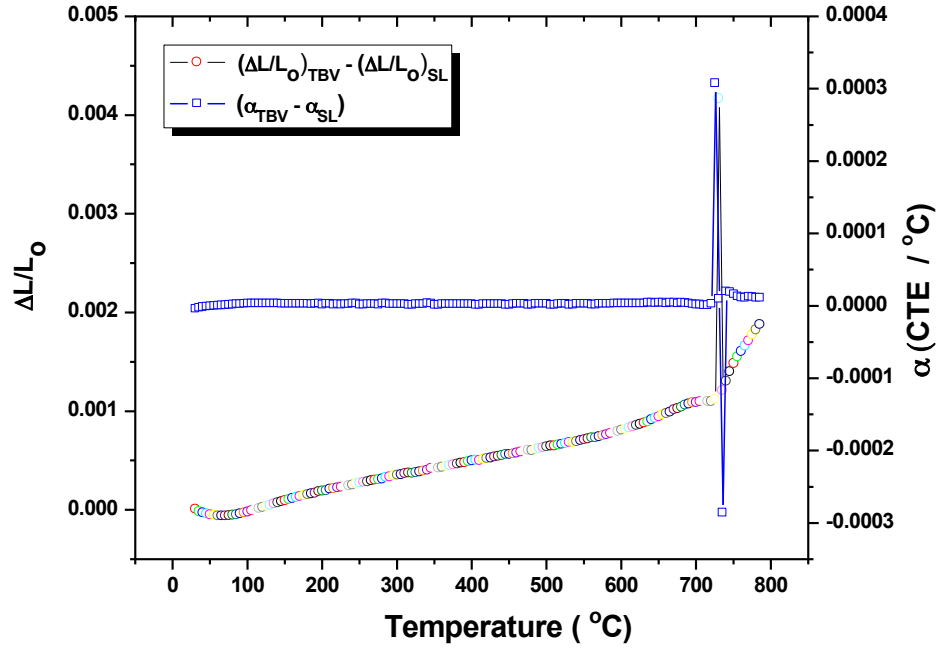


Figure 5.15 (c): Difference between coefficient of thermal expansion (α) for TBV and SL glass with respect to temperature.

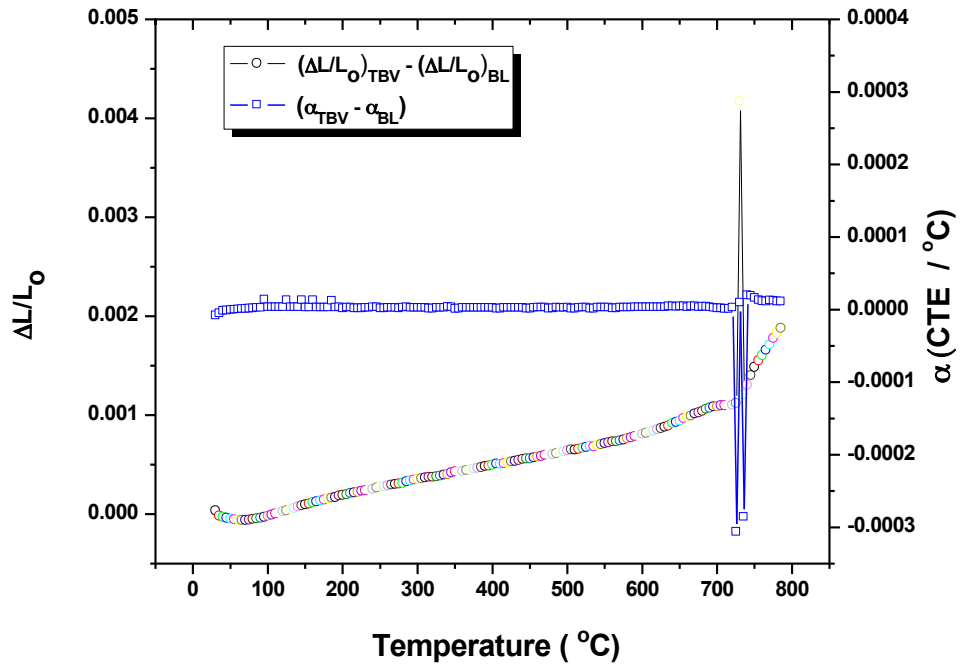


Figure 5.15 (d): Difference between coefficient of thermal expansion (α) for TBV and BL glass with respect to temperature.

5.4.1 ML/TBV diffusion couples

Fig. 5.16 (a) shows the interface of ML/TBV diffusion couple heat-treated at 800 °C for 5 h. Good adhesion between ML glass and intermediate TBV could be seen at the interface. The interface region in glass side is smooth and free from pores. The absence of any corrosion between electrolyte and glass at interface could be further confirmed from the X-ray dot-mapping as shown in fig. 5.16 (b). The X-ray dot mapping completely precludes the segregation of elements. The degree of brightness indicates the distribution pattern as well as concentration of elements. After 100 h heat-treatment of ML/TBV couple at 800 °C, the SEM cross-section has revealed pores at the interface as seen in fig. 5.17 (a) though no undesirable reaction products are seen at the interface. From the dot-mapping (fig. 5.17 (b)), it is clear that titanium and magnesium has diffused in considerable amount. It may be ascribed due to their small ionic radii. Bismuth has also migrated to some extent towards glass side, but the diffusion kinetics is very slow for such heavy ions.

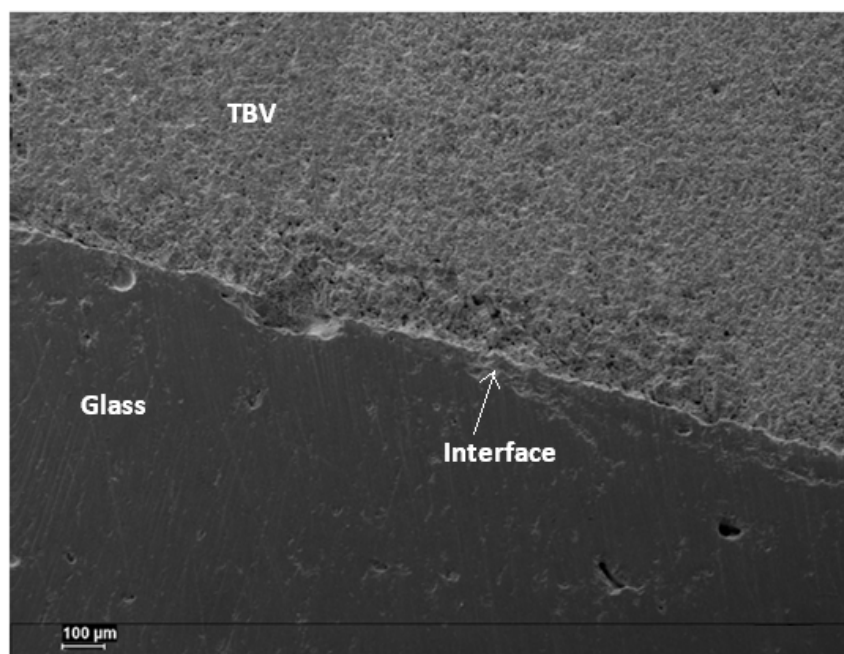


Figure 5.16 (a): ML/TBV diffusion couple at 800 °C for 5 h.

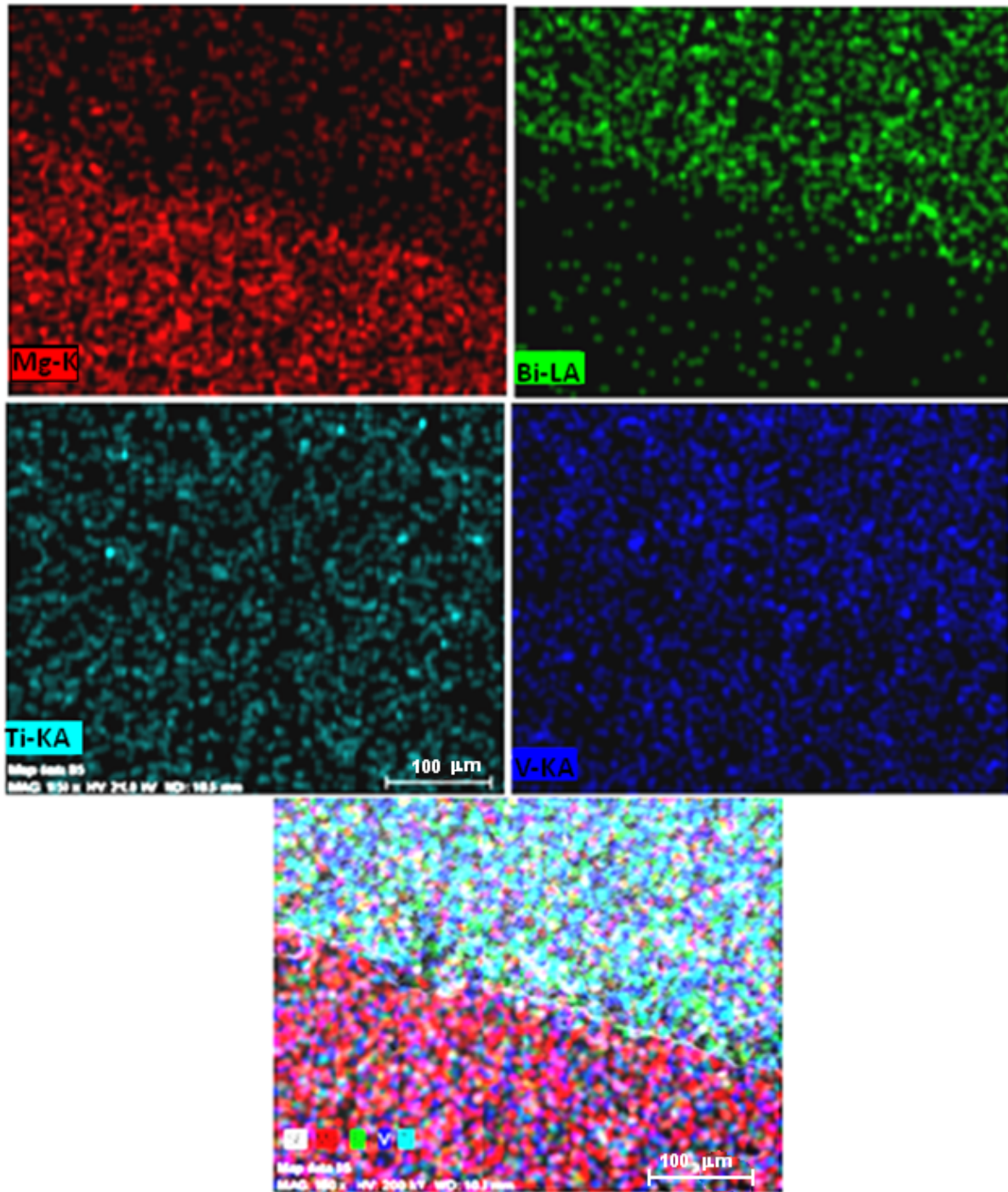


Figure 5.16 (b): X-ray dot mapping of ML/TBV diffusion couple at 800 °C for 5 h.

The central region of cross-section of ML/TBV diffusion couple heat-treated at 800 °C for 750 h is shown in fig. 5.18 (a). Some cracks are observed at the interface. In the interior region of the glass, some pits and pores could be seen. The appearance of closed pits (porosity) usually

does not lead to increase of leak rate [56]. Moreover, no accumulation of elements around the pits is observed as can be seen from EPMA (fig. 5.18 (b)) along the interface. Oscillations are observed in concentration profiles for all the elements. The possible reasons, which are assigned, to these oscillations include low density and concentration of elements, compositional difference between devitrified and glassy phase and interaction among X-rays of different elements [57]. Each curve is the relative distribution of specific element instead of absolute content in the system. The concentration of every element has dropped at the interface, indicating discontinuity at the joint region. Though titanium has again diffused from the electrolyte matrix to great extent. However, vanadium profile reveals highest diffusion concentration beyond the interface among all the elements bismuth concentration profile follows S-shaped curve [58-59]. The spikes are very small in bismuth profile beyond the interface which indicates homogenous diffusion. Moreover, the diffusion of bismuth is lowest among all the elements. It may be attributed to its larger size and high atomic mass.

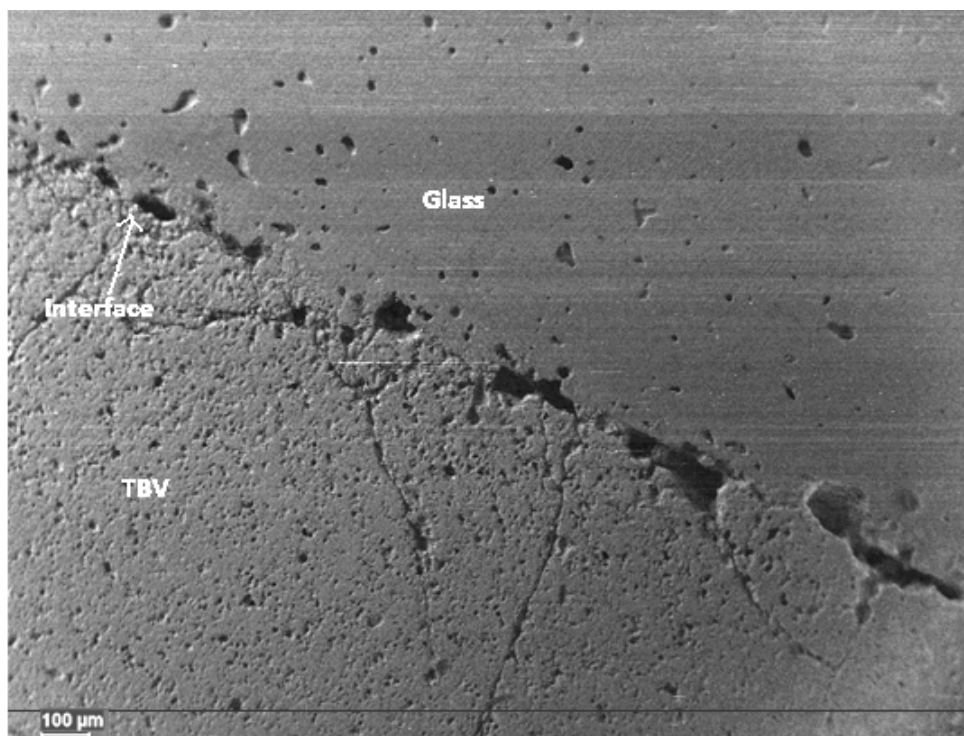


Figure 5.17 (a): ML/TBV diffusion couple at 800 °C for 100 h.

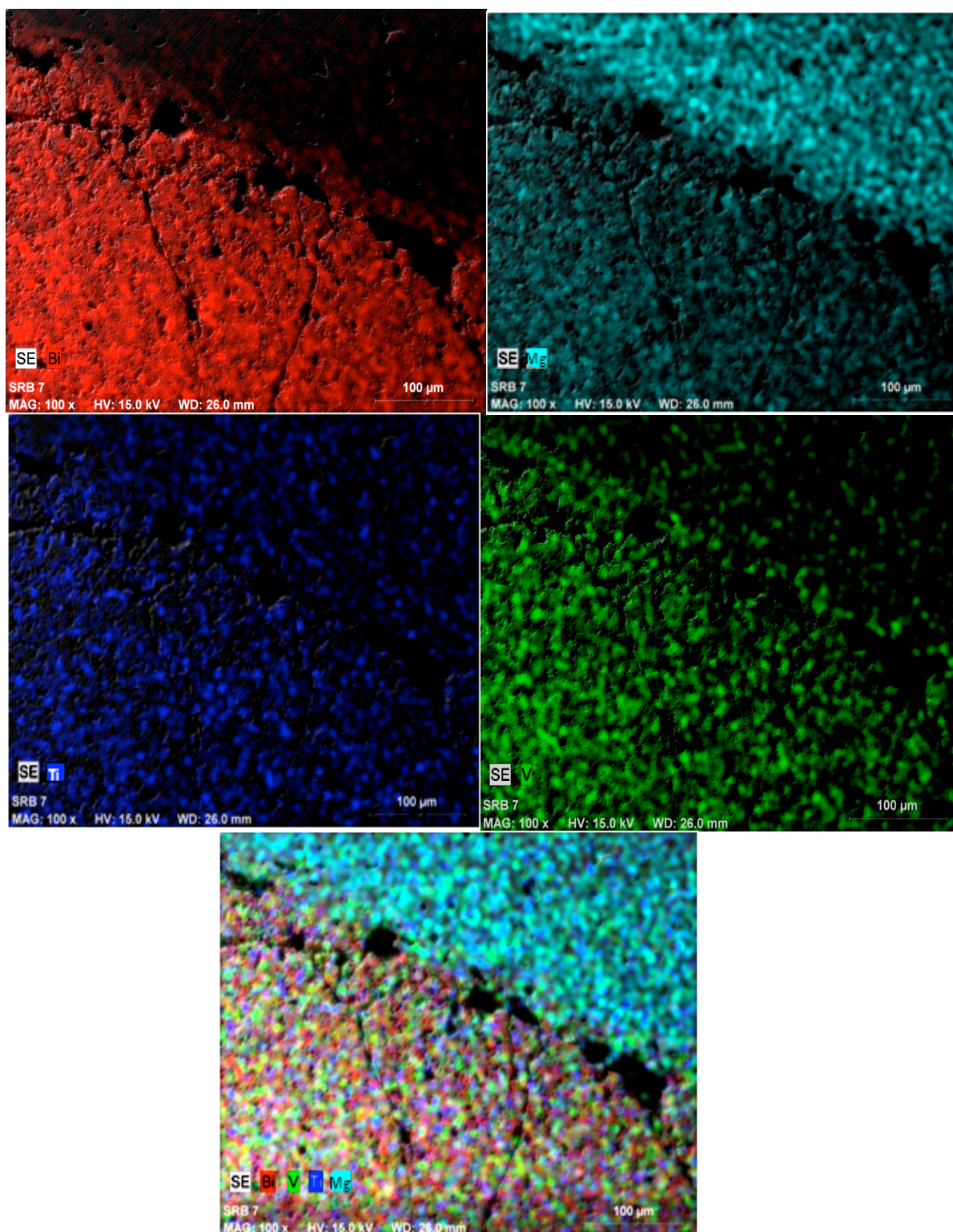


Figure 5.17 (b): X-ray dot mapping of ML/TBV diffusion couple at 800 °C for 100 h.

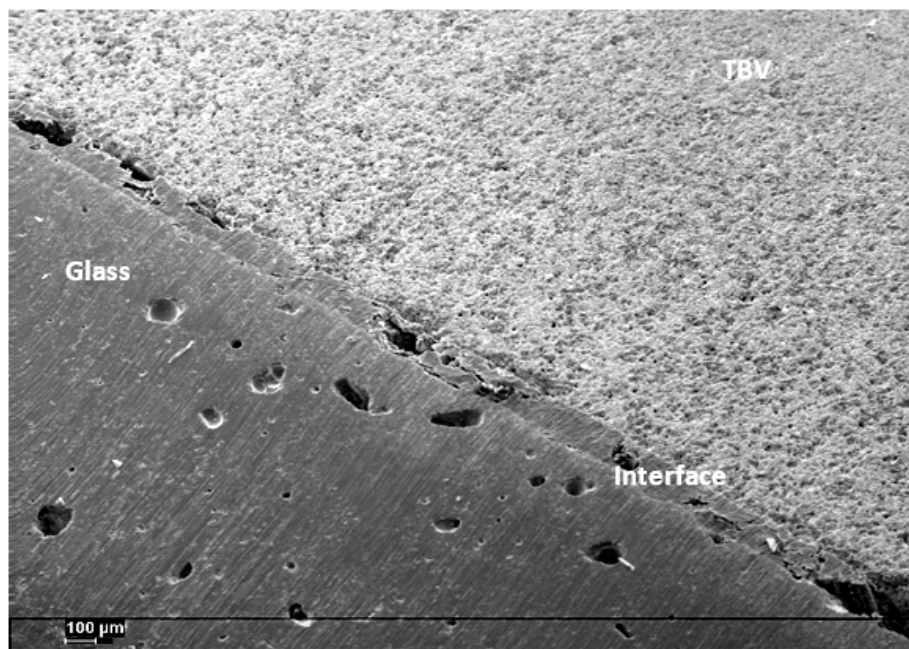


Figure 5.18 (a): ML/TBV diffusion couple at 800 °C for 750 h.

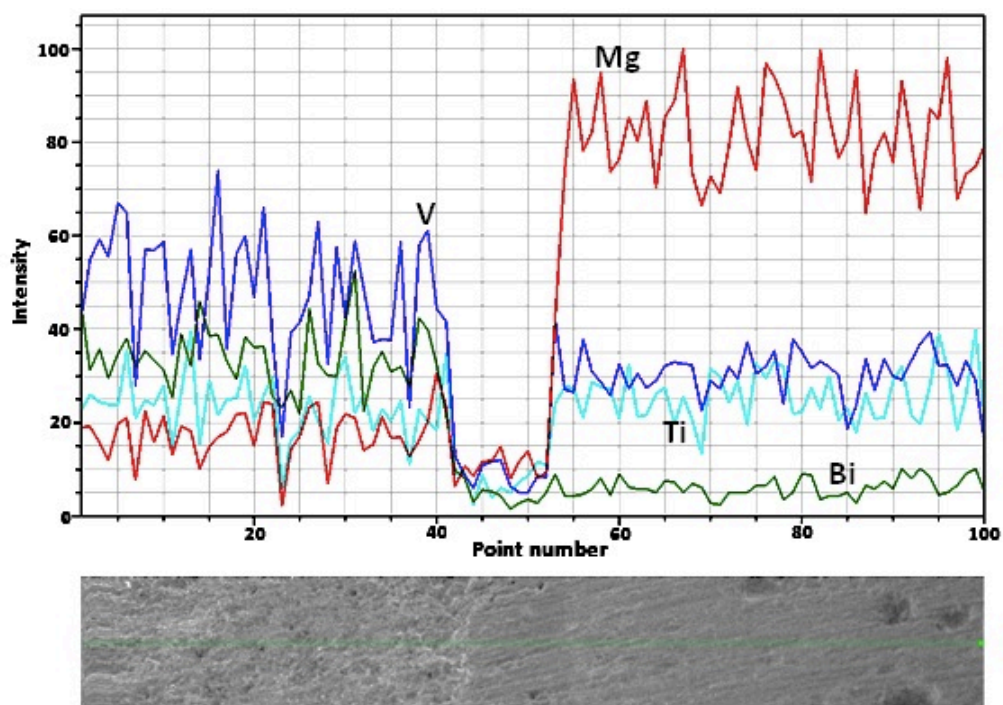


Figure 5.18 (b): EPMA of ML/TBV diffusion couple at 800 °C for 750 h.

The microstructure of TBV after 750 h heat-treatment has been given in fig. 5.19. The average grain size is 7.74 μm with standard deviation of 1.51 and variance 2.28. Some porosity could also be seen in the microstructure.

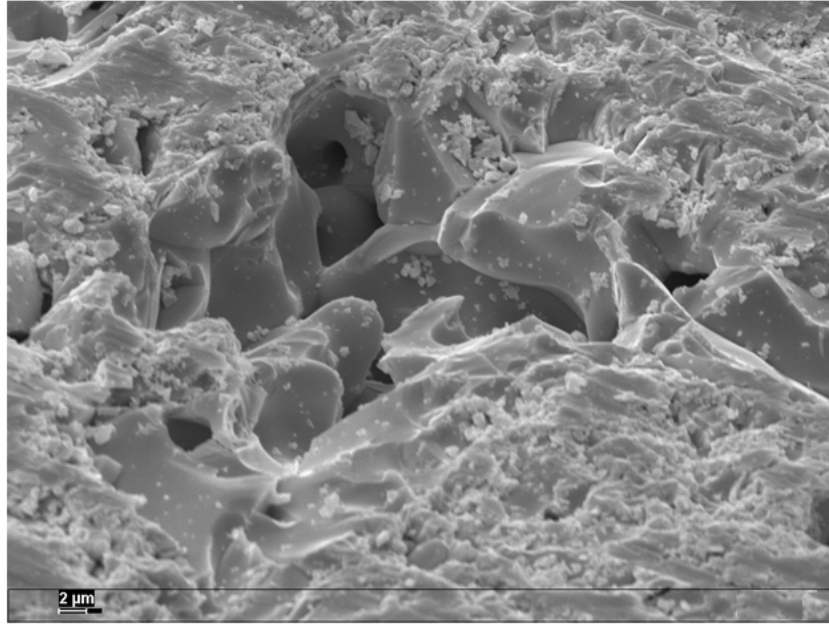


Figure 5.19: Microstructure of TBV electrolyte after 750 h treatment.

5.4.2 CL/TBV diffusion couples

Fig. 5.20 (a) shows the diffusion couple of CL/TBV after 5 h heat-treatment at 800 °C. The scan of joint cross-section reveals homogenous microstructure across the sealing region. The interface is smooth and pore free. This observation is also supported by X-ray dot mapping (fig. 5.20 (b)).

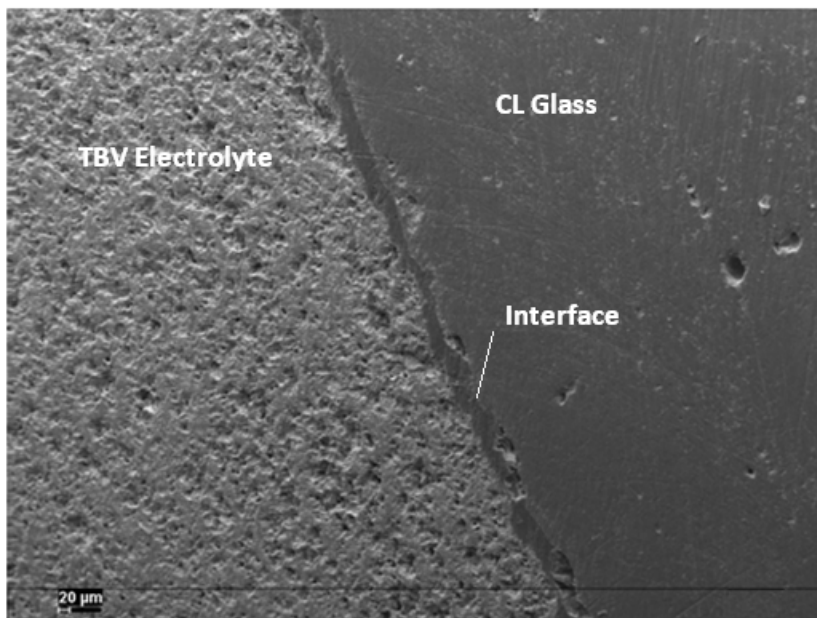


Figure 5.20(a): CL/TBV diffusion couple at 800 °C for 5 h.

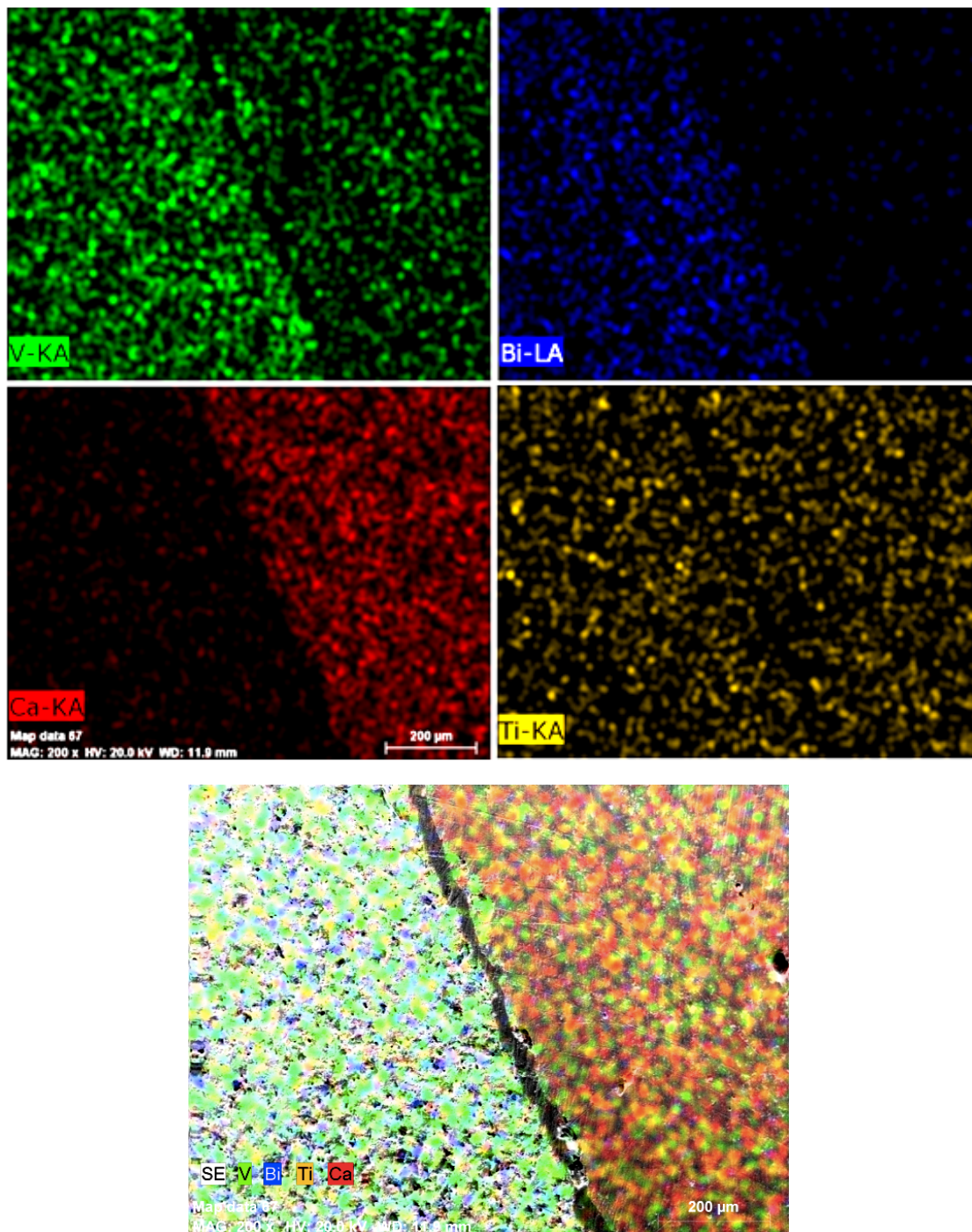


Figure 5.20 (b): X-ray dot mapping of CL/TBV diffusion couple at 800 °C for 5 h.

The diffusion of V^{5+} and Ti^{3+} is more as compared to Bi^{3+} . It is due to smaller ionic radii of these cations as compared to Bi^{3+} [60]. On the other hand, the diffusion of modifier cation like Ca^{2+} , from the glass side is non-significant. Even after 100 h treatment at 800 °C (fig. 5.21 (a)), the interface is without cracks and moreover no reaction products have been observed at the interface. Pit formation could not be observed in the glass region. Very good bonding

characteristics have been observed in the sealing region, which are further supported by EPMA (fig. 5.21(b)). The concentration of vanadium is highest at the interface as shown by the EPMA results. Bismuth follows S-shaped curve along with minimum diffusion, whereas calcium follows Z-shaped curve. Titanium diffused in considerable extent on glass side of the interface. After 750 h treatment at 800 °C, the CL/TBV has shown structural integrity as depicted by fig. 5.22 (a). The interface is found to be continuous and defect free. However, some pit formation could be observed in the glass region, which is generally attributed to entrapped volatility of gases etc. The diffusion of titanium and vanadium is also seen in X-ray dot mapping (fig. 5.22 (b)). Titanium occupies defect sites in TBV and comes out easily from the lattice after achieving sufficient thermal energy [1-3, 61]. Interestingly, the diffusion of calcium and bismuth has decreased with increasing heat-treatment duration. Most important, brittle silicide and boride phases have not been observed in both XRD and microstructural analysis. Coupled glass with TBV have shown the precipitation of Ca_2SiO_4 phase whose CTE lies in between $(10-14) \times 10^{-6} / ^\circ\text{C}$ [62-63], which is very close to reported CTE values i.e. $10.25 \times 10^{-6} / ^\circ\text{C}$ for TBV. The thermal mismatching is not significant, which minimizes the stress and increases the endurance of seal in IT-SOFC environment.

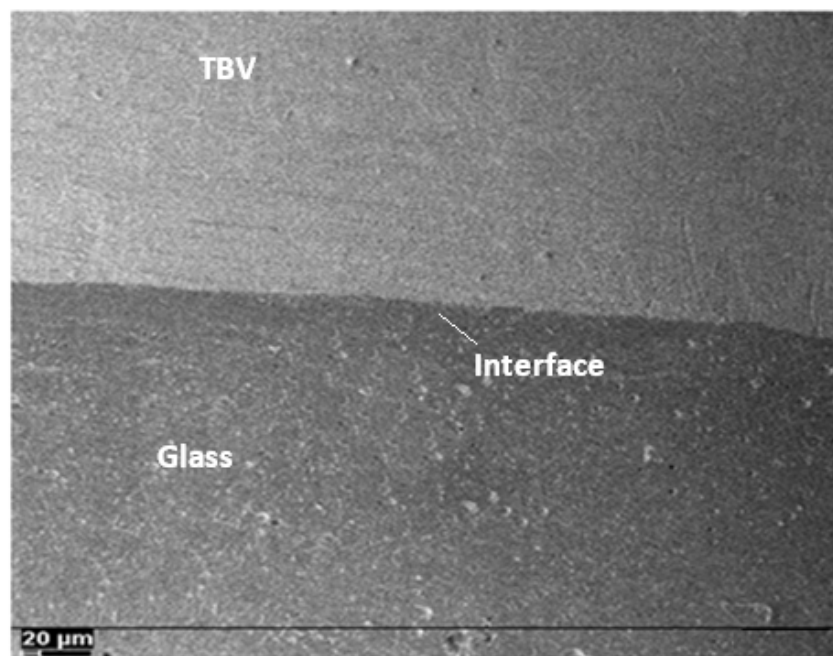


Figure 5.21(a): CL/TBV diffusion couple at 800 °C for 100 h.

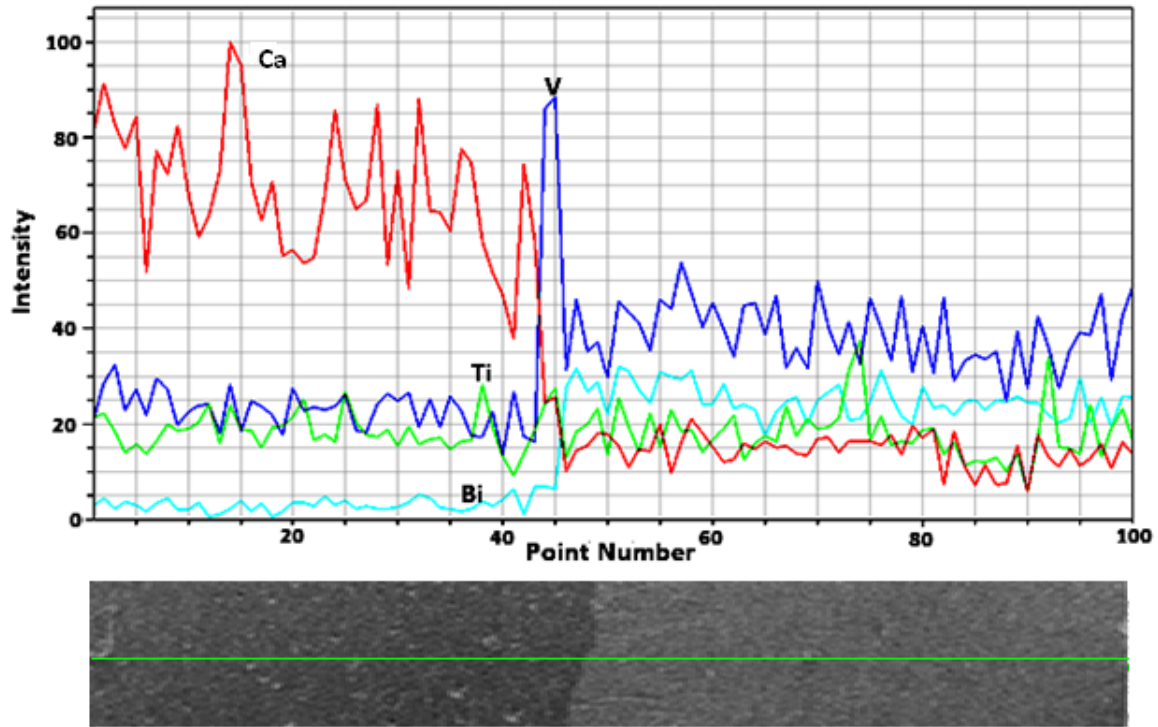


Figure 5.21(b): EPMA of CL/TBV diffusion couple at 800 °C for 100 h.

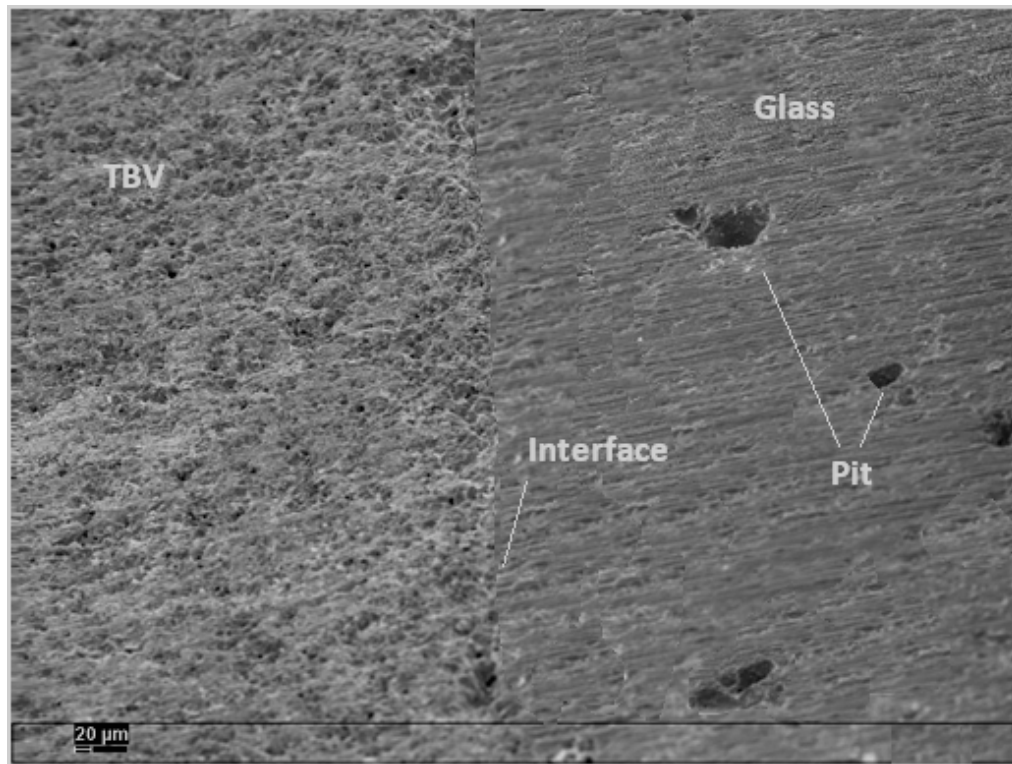


Figure 5.22 (a): CL/TBV diffusion couple at 800 °C for 750 h.

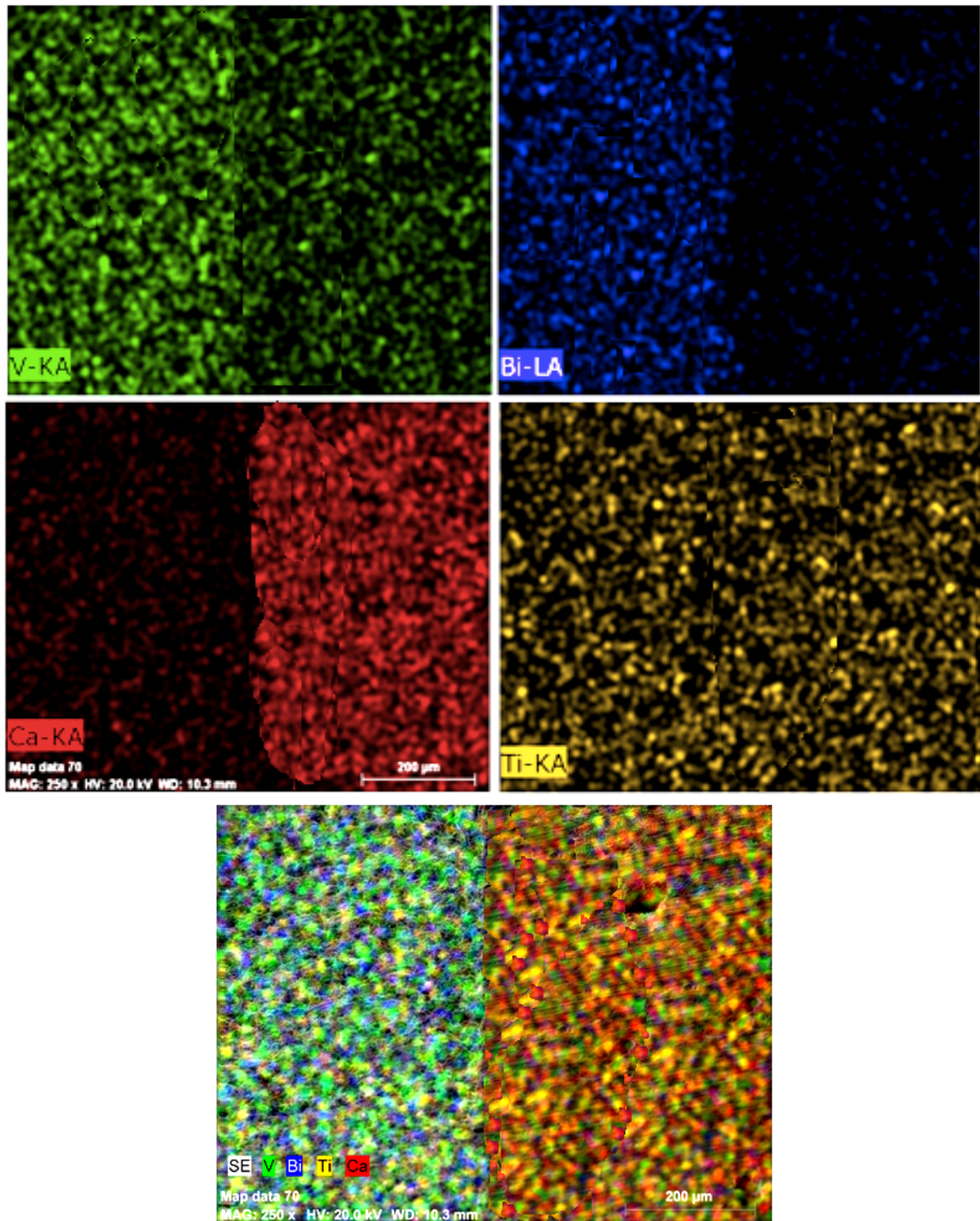


Figure 5.22 (b): X-ray dot mapping of CL/TBV diffusion couple at 800 °C for 750 h.

5.4.3 SL/TBV diffusion couples

Fig. 5.23 (a) shows the diffusion couple of SL/TBV after 5 h heat-treatment at 800 °C. The joined couple is sectioned at the middle and interface is analysed by SEM. The sealing glass is well-bonded to TBV electrolyte. Moreover, interface is free of any elemental segregation. Porosity could be seen in the SL glass side, which is attributed to amorphousness present in glass after heat-treatment of 5 h as observed in XRD (fig. 5.11). Generally, the amorphous content of glass contributes to its internal brittleness. Furthermore, the internal brittleness of glass subsequently, lead to pit formation. X-ray dot mapping (fig. 5.23 (b)) indicates considerable diffusion of vanadium and titanium from electrolyte. Bismuth and strontium has diffused negligibly due to their larger sizes and ionic radii. After 100 h treatment at 800 °C (fig. 5.24 (a)), uniform and homogenous microstructure has been observed on either side of interface along with very good bonding characteristics. The glass is totally free of porosity and cracks. No separation or interaction layer between the SL and TBV has been detected which is further supported by EPMA results (fig. 5.24 (b)). The relative intensity distribution of elements is observed in the form of composition spikes. Titanium has diffused to considerable extent on either side of interface. Very similar observation has been made even in CL/ TBV diffusion couple. Strontium follows ‘S’ shaped concentration profile, whereas ‘Z’ profile is followed by bismuth and vanadium. Bismuth has shown minimum diffusion among all other elements towards either side of interface.

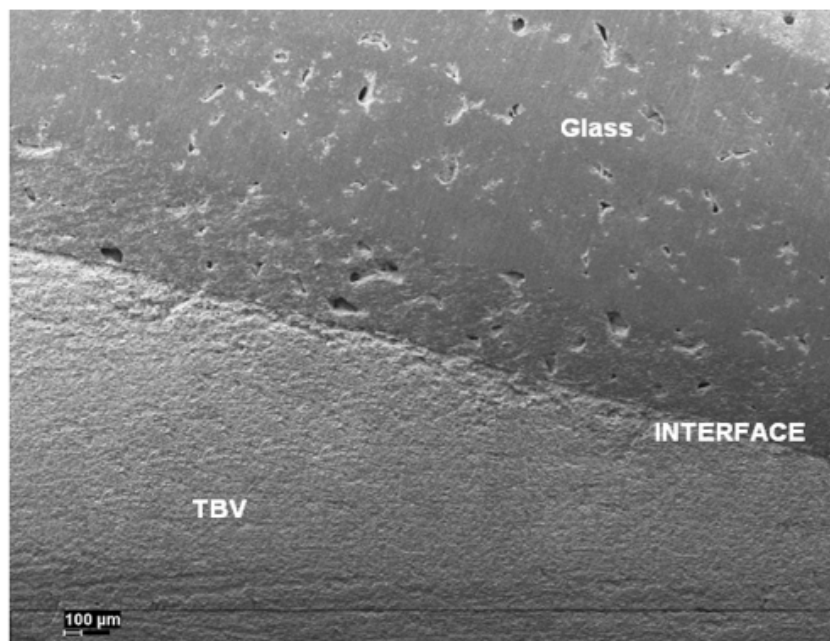


Figure 5.23 (a): SL/TBV diffusion couple at 800 °C for 5 h.

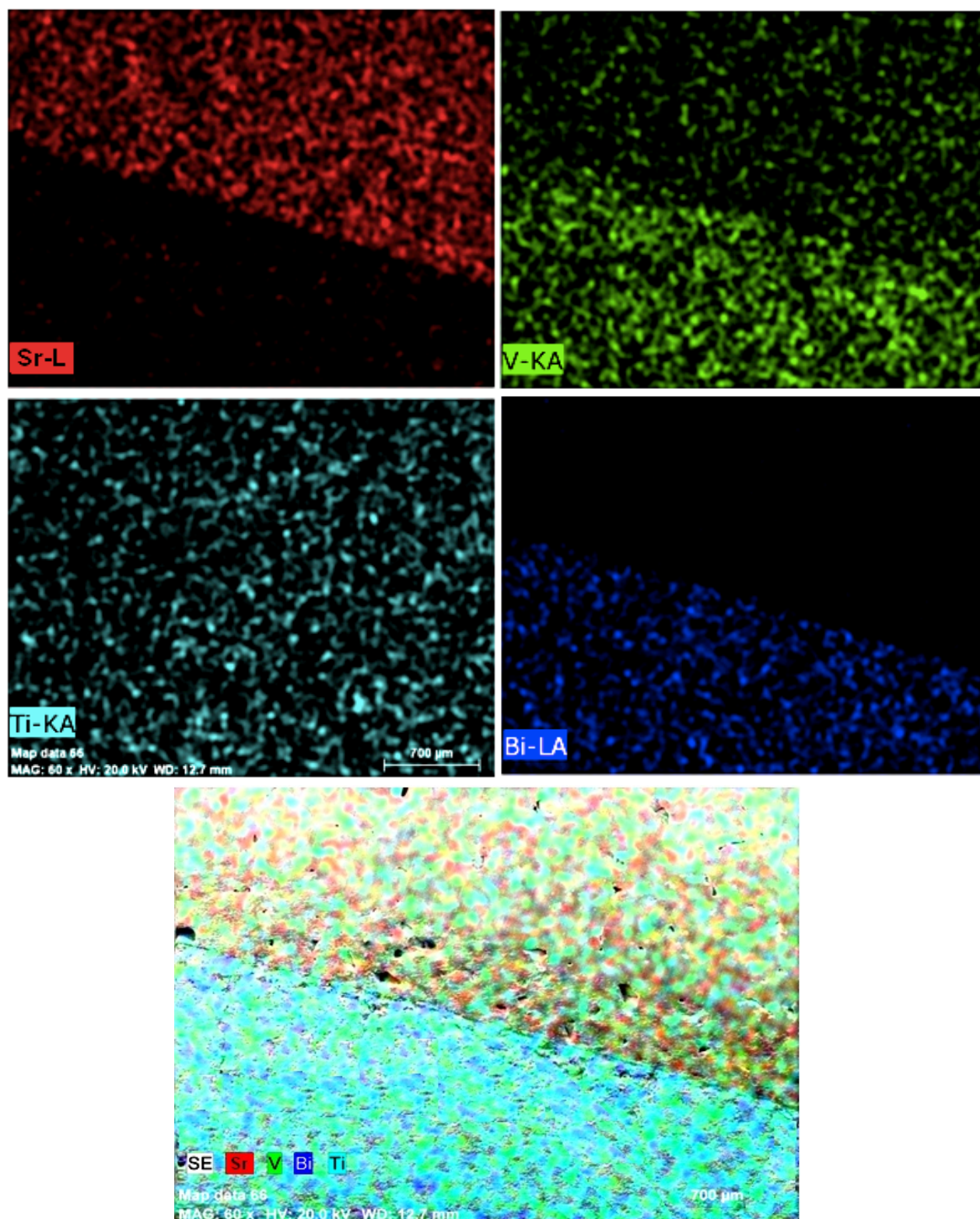


Figure 5.23(b): X-ray dot mapping of SL/TBV diffusion couple at 800 °C for 5 h.

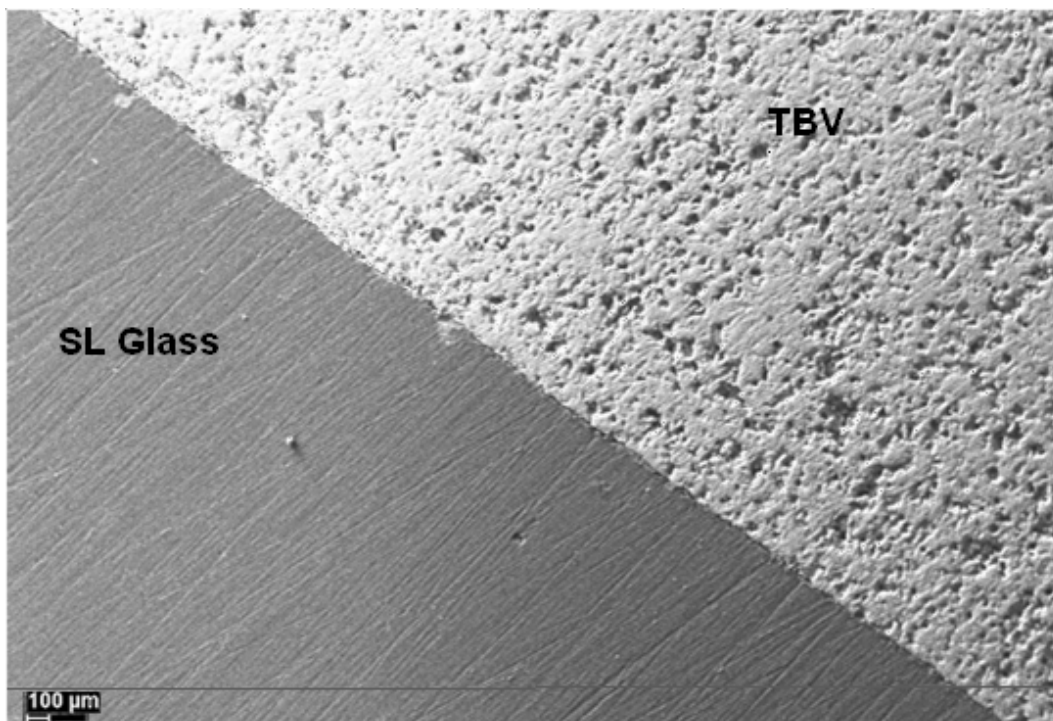


Figure 5.24 (a): SL/TBV diffusion couple at 800 °C for 100 h.

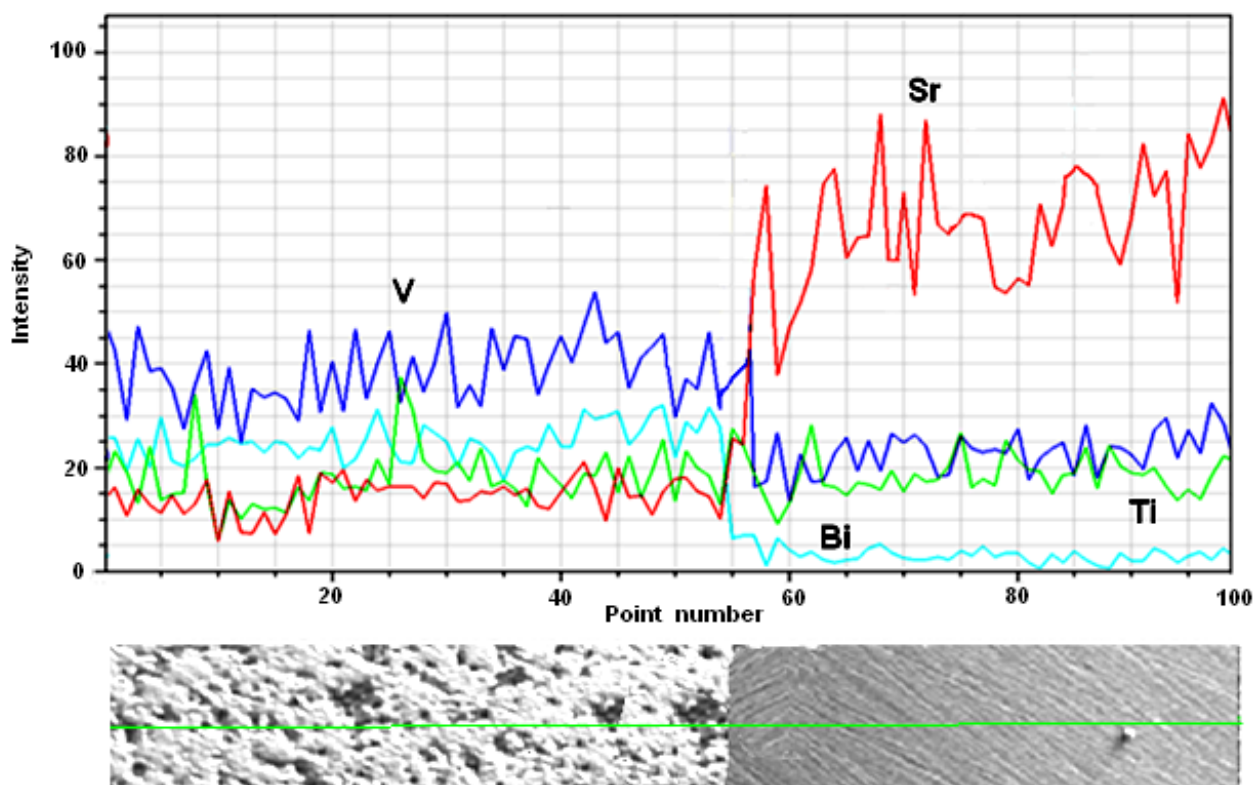


Figure 5.24 (b): EPMA of SL/TBV diffusion couple at 800 °C for 100 h.

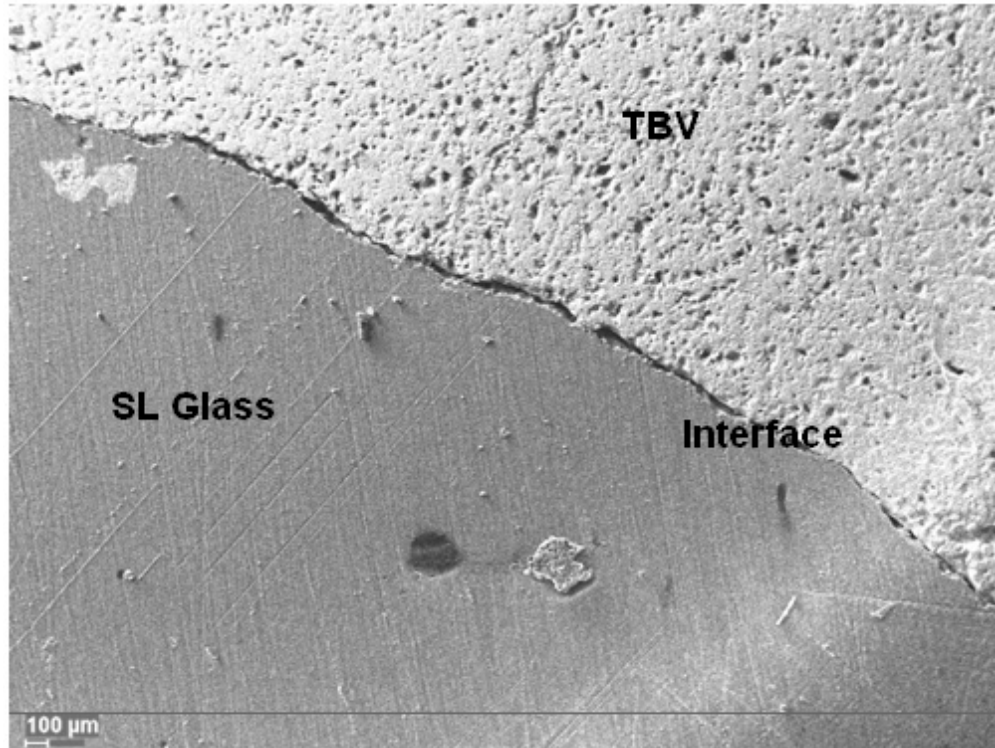


Figure 5.25 (a): SL/TBV diffusion couple at 800 °C for 750 h.

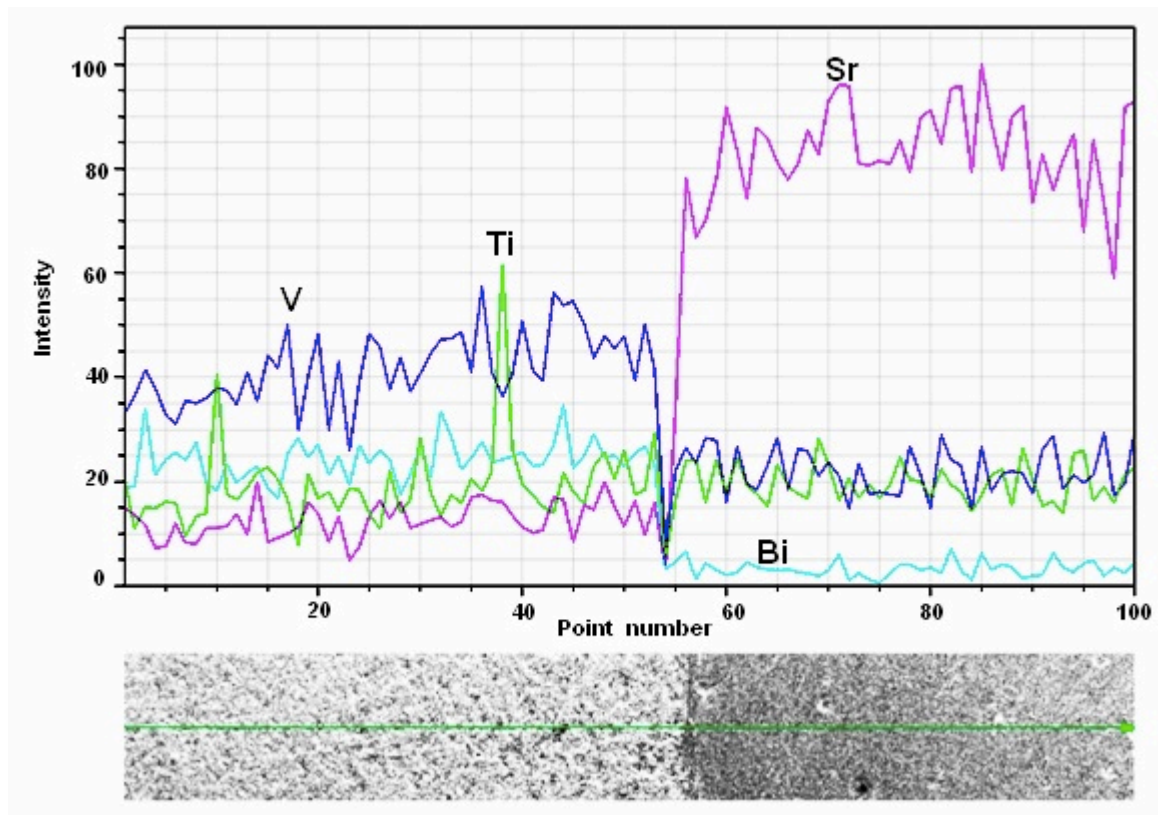


Figure 5.25 (b): EPMA of SL/TBV diffusion couple at 800 °C for 750 h.

Absence of extensive diffusion of elements suggests that SL glass and its interface with TBV are thermochemically stable. Thus, good thermochemical compatibility is exhibited even after 100 h heat-treatment. After 750 h treatment at 800 °C, the SL/TBV has shown lower structural integrity as indicated in fig. 5.25 (a). Delamination at the interface could be seen, though no reaction or corrosion products could be seen. The diffusion of titanium and vanadium could again be observed as shown by EPMA (fig. 5.25(b)). Additionally, the EPMA shows sudden decrease followed by increase in compositional spikes for all the elements at the interface. Hence, ‘S’ or ‘Z’ shaped profiles are no longer followed by the elements. This indicates loss of structural integrity for the diffusion couple after prolonged heat-treatment. Coupled SL glass with TBV has shown the precipitation of $\text{Sr}_3\text{Si}_3\text{O}_9$ and pyrochlore $\text{La}_2\text{Si}_2\text{O}_7$ which are stable phases [51, 64]. In general, strontium silicate phases have low CTE [63]. This delamination could have been due to CTE mismatch developed due to thermal stresses at the interface.

5.4.4 BL/TBV diffusion couples

The SEM microphotographs of glass/TBV diffusion couple heat-treated at 800 °C for 5, 100 and 750 h are shown in figs. 5.26, 5.27 and 5.28, respectively. The BL glass exhibits fairly homogenous microstructure and no severe corrosion effects at the interface are observed as can be seen in fig. 5.26 (a).

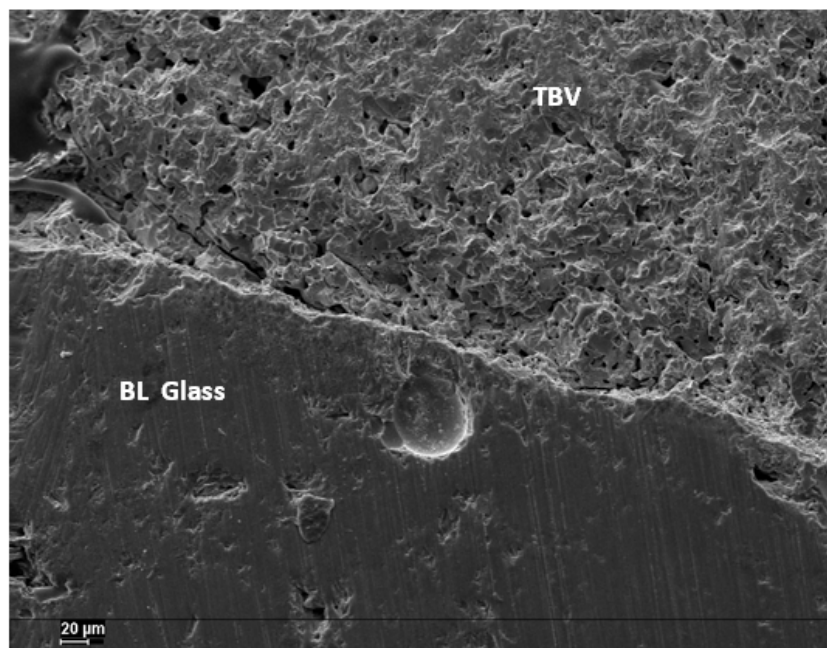


Figure 5.26 (a): BL/TBV diffusion couple at 800 °C for 5 h.

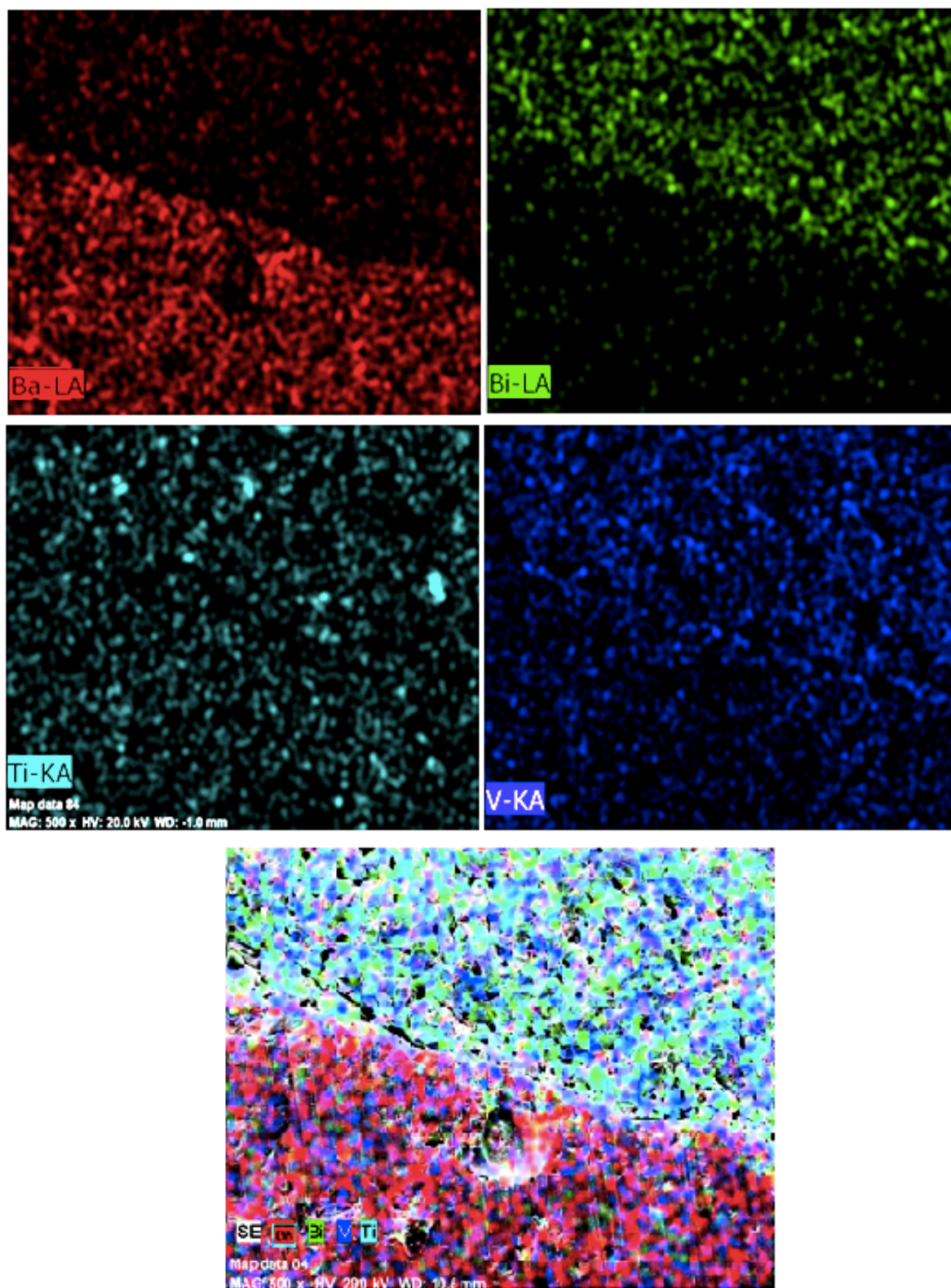


Figure 5.26 (b): X-ray dot mapping of BL/TBV diffusion couple at 800 °C for 5 h.

Preliminary studies indicate good adhesion without any gap at the interface between glass and electrolyte. From X-ray dot mapping (fig. 5.26 (b)), it is clear that very low amount of barium and bismuth diffusion has occurred on either side of interface, which can be attributed to their large ionic radii. Porosity in BL glass is also observed which also propagated within the bulk glass after 100 h treatment as can be seen in fig. 5.27, though no delamination occurred. Interfacial delamination cracks between sealant and cell component must be avoided as they can act as preferential path for fuel transport. This porosity is, generally, due to presence of amorphous content. The activation energy of BL glass is large, hence the crystallized fraction is absent in this glass even after 100 h treatment. Interesting result has been obtained after 750 h treatment. The pore size decreased as evident from fig. 5.28 (a). This could be due to the self-healing ability of BL glass. BL glass have demonstrated self-healing close to the cell operating temperature of 800 °C as well as remained stable against crystallization for a long time. Glasses which possess small amount of the crystalline phases and long-term stability against crystallization are potential candidates for making self-healing glass seals. The presence of glassy matrix in glass ceramic shows self-healing behavior during SOFC operation. BL glass has quite large amorphous glassy phase even after heat-treatment.

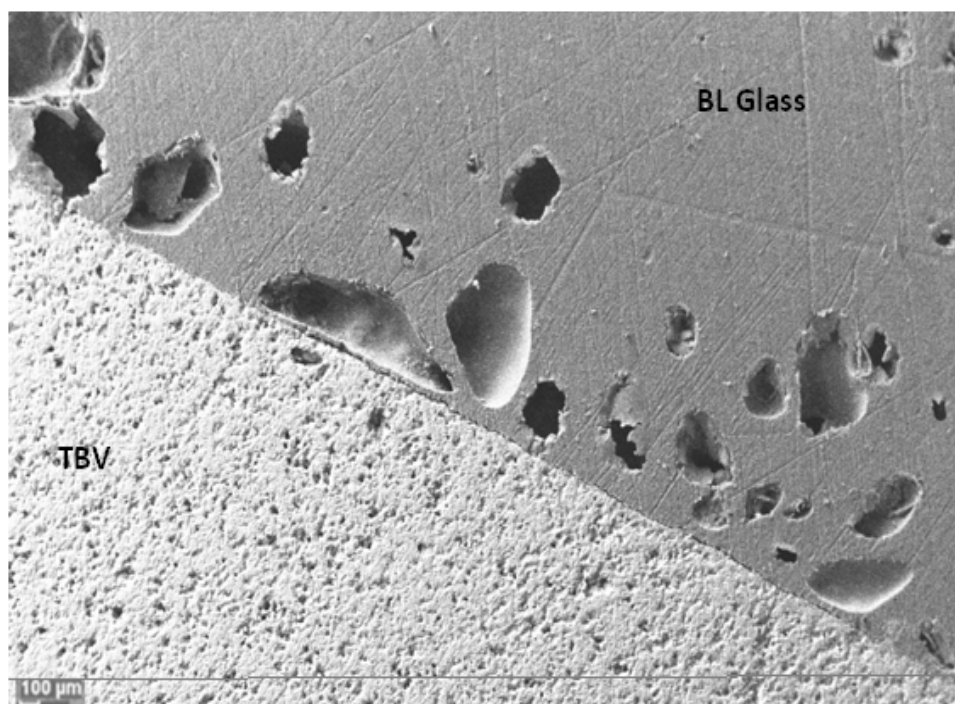


Figure 5.27: BL/TBV glass diffusion couple at 800 °C for 100 h.

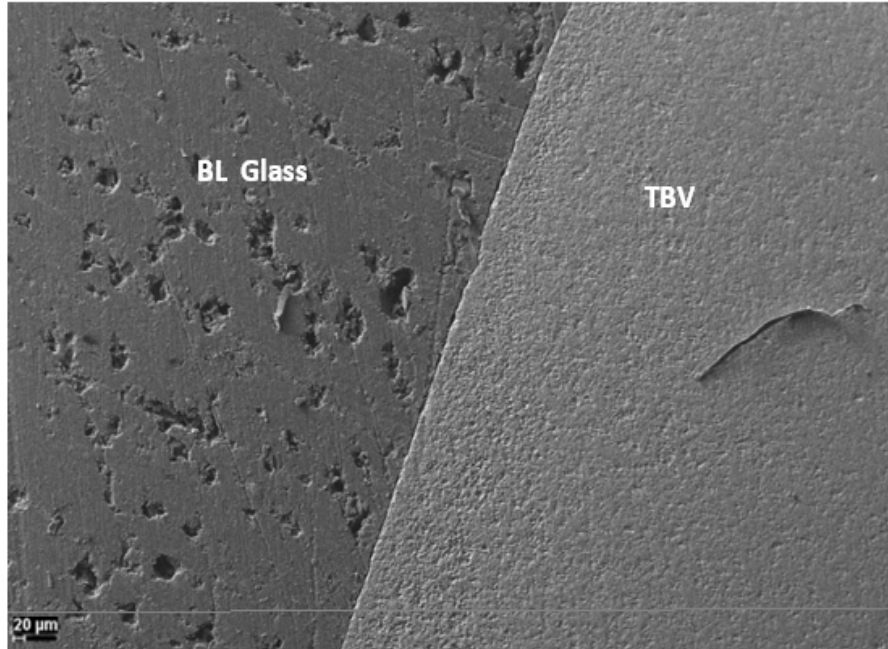


Figure 5.28 (a): BL/TBV diffusion couple at 800 °C for 750 h.

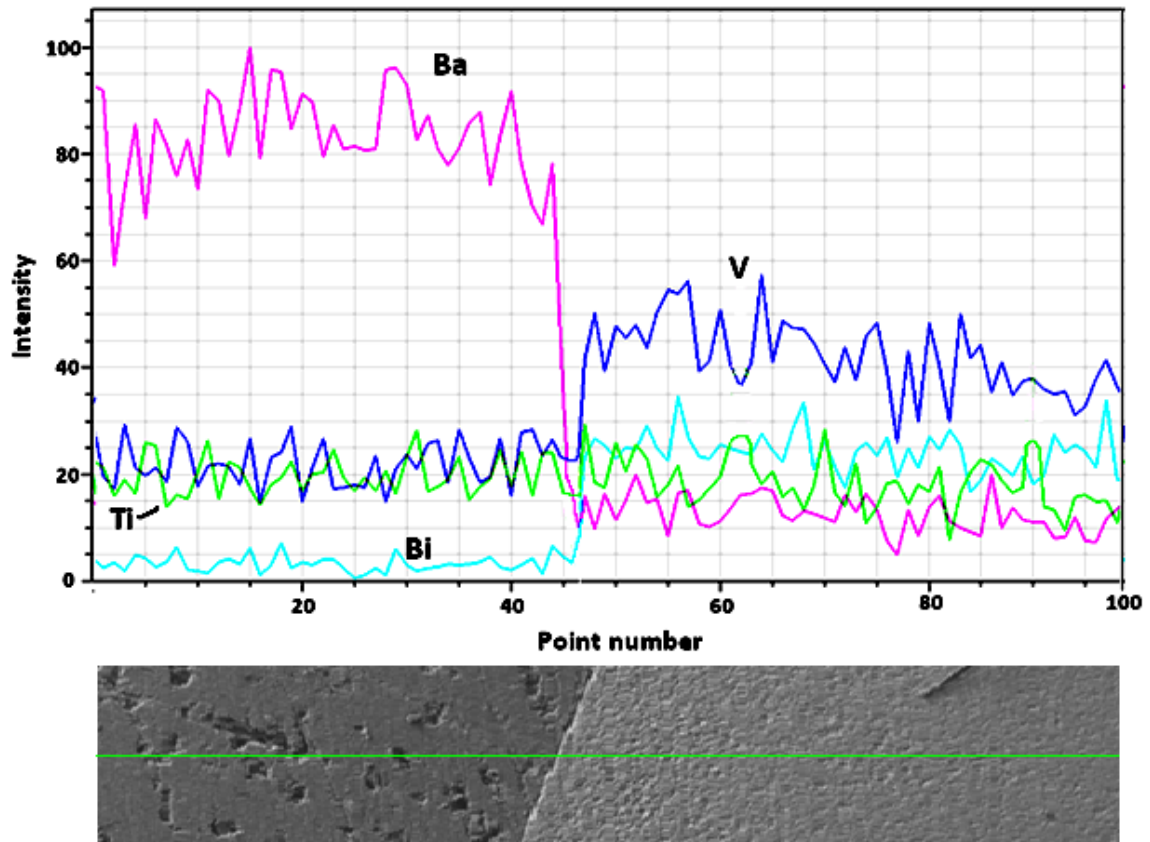


Figure 5.28 (b): EPMA of BL/TBV diffusion couple at 800 °C for 750 h.

Materials having slightly different CTE can be used for seals when induced thermo-mechanical stresses get relaxed at the cell operating temperature,. Appreciable amount of vanadium and titanium diffusion could be seen into the glass ceramic as is evident in fig. 5.28(b). The Ba^{2+} ions have also diffused from the glass matrix. Titania-rich zone could not be seen along the interface in any of the diffusion couple, indicating absence of any adverse reaction. Titania based phases are generally brittle in nature. This condition is highly favourable for sealing applications.

5.5 Sealing and microstructural analysis of glasses with high temperature YSZ

5.5.1 ML/YSZ diffusion couples

Fig. 5.29 (a) shows the SEM micrograph of ML/YSZ sample heat-treated at 850 °C for 5 h in air. Examination around the seal region has depicted very good adhesion within ML glass and YSZ electrolyte. The interior of glass region has shown residual porosity which can be related to tensile thermal stress generated by CTE mismatch between glass and electrolyte. No structural modifications have been observed at the interface. As is evident from elemental dot mapping (fig. 5.29 (b)), the diffusion of Y^{3+} and Mg^{2+} has occurred to considerable extent on both sides of interface. Similarly, some diffusion of Zr^{4+} could also be seen. Fig. 5.30 (a) shows the interface of ML/YSZ couple heat-treated at 850 °C for 100 h. After 100 h treatment, the interface still remains intact and free from any gaps or cracks. No detrimental reaction products have been observed at interface. Porosity could be seen in the glass side. This could be due to amorphousness present in glass even after heat-treatment of 100 h as observed in XRD (fig. 5.8). The amorphous content in the glass contributes to the internal brittleness. This internal brittleness could have subsequently lead to pit formation which are observed in the central part of glass. Furthermore, the cross-section of this couple was analyzed using X-ray dot mapping (fig. 5.30 (b)) indicated diffusion of Mg^{2+} ion towards the electrolyte side. In addition to this, yttrium also diffused from electrolyte and migrated towards glass matrix. But the diffusion of zirconium towards either side of interface is less as compared to similar diffusion couple heat-treated for 5 h at 850 °C.

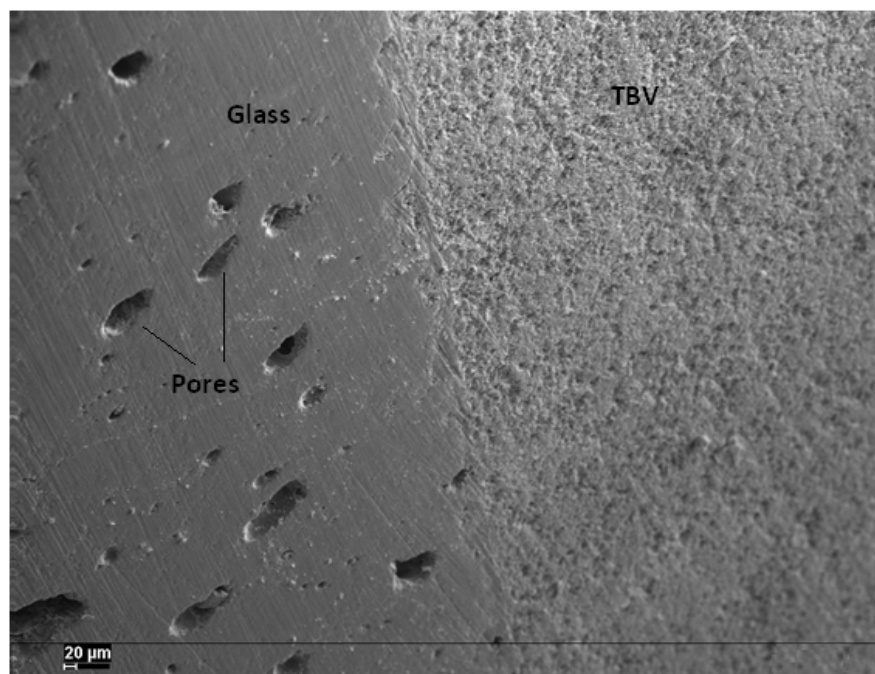


Figure 5.29(a): ML/YSZ diffusion couple at 850 °C for 5 h.

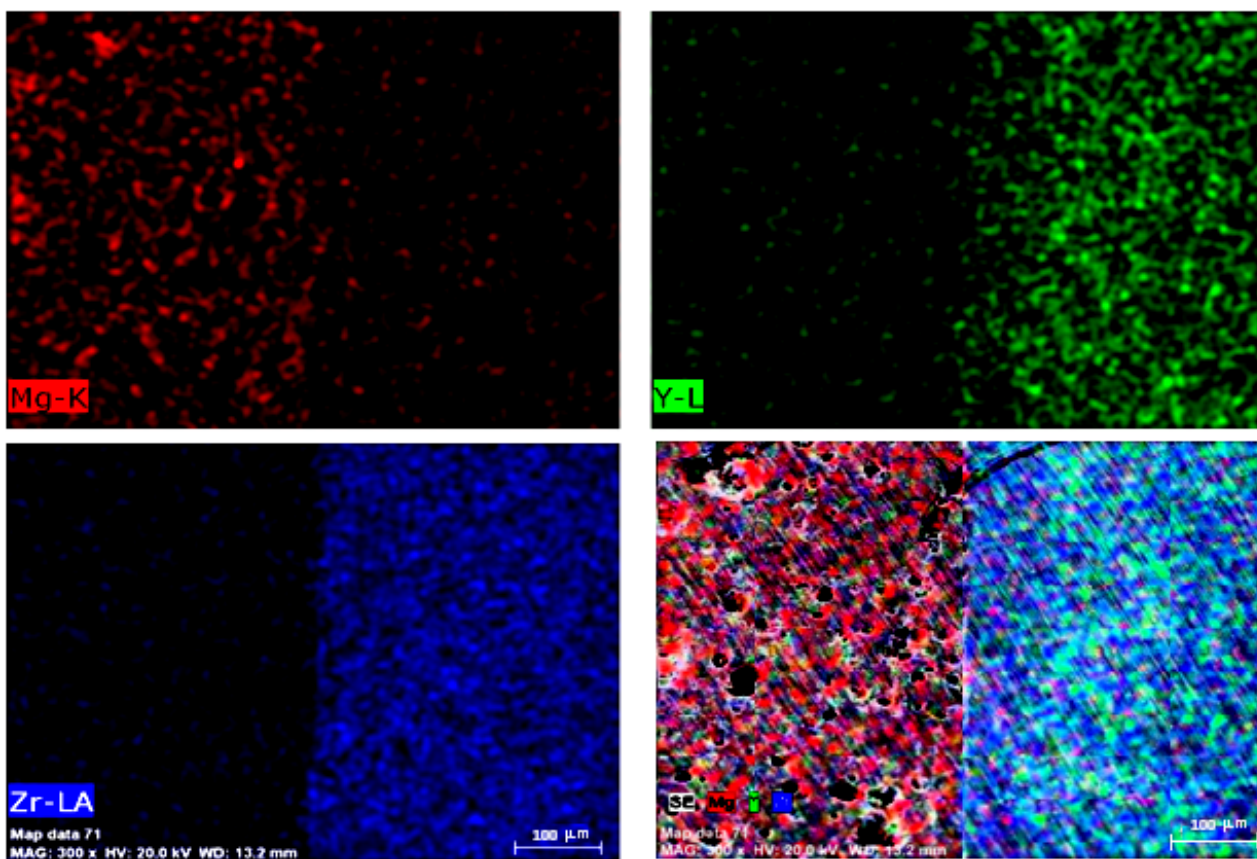


Figure 5.29 (b): X-ray dot mapping of ML/YSZ diffusion couple at 850 °C for 5 h.

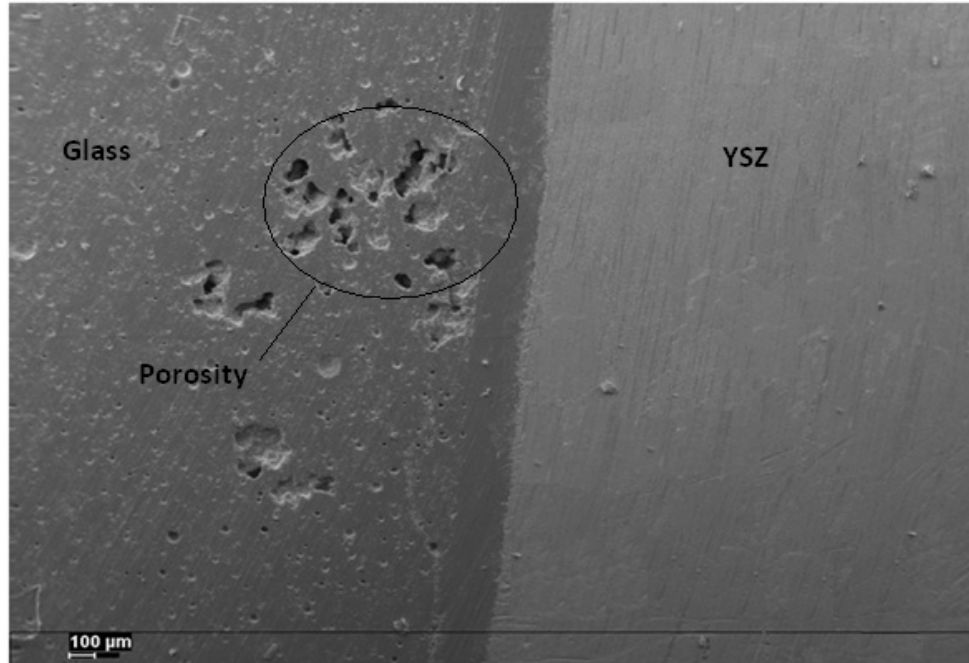


Figure 5.30: (a) ML/YSZ diffusion couple at 850 °C for 100 h.

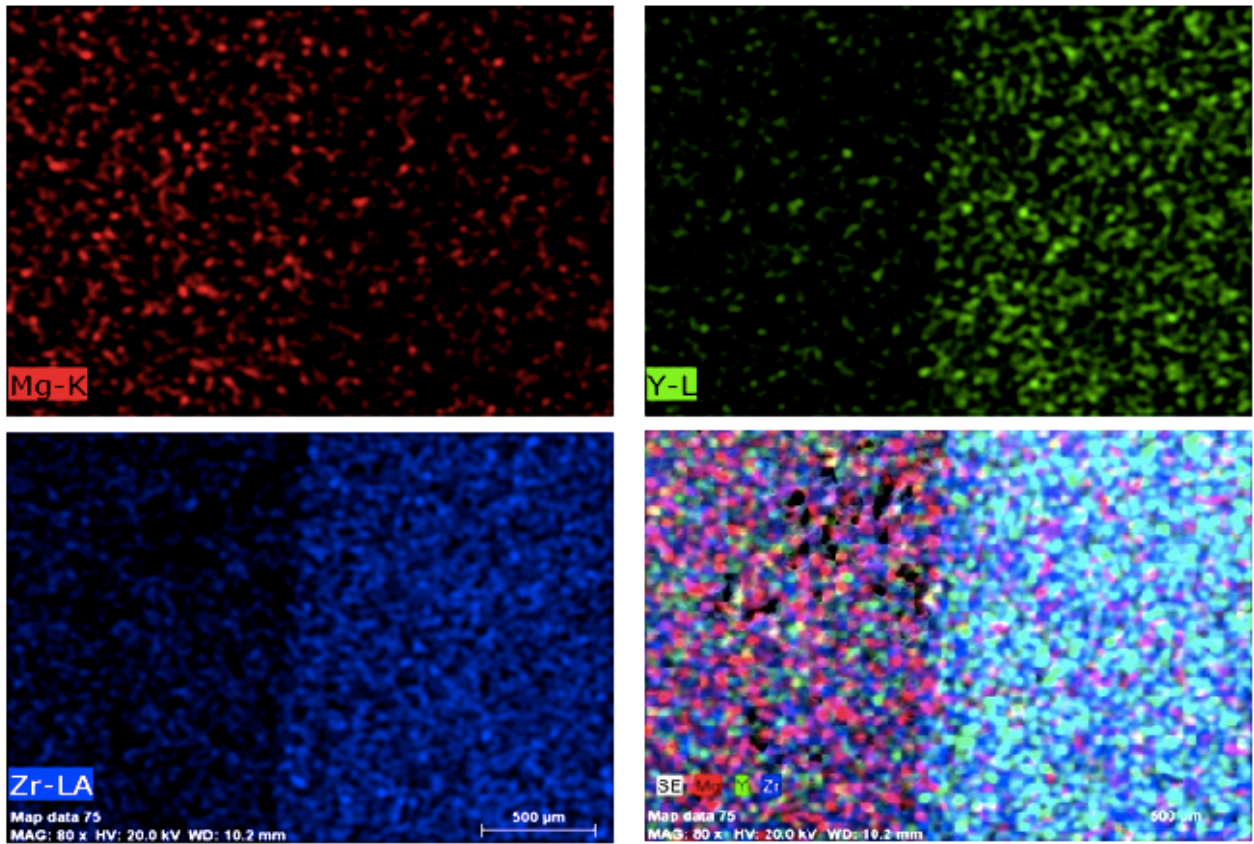


Figure 5.30 (b): X-ray dot mapping of ML/YSZ diffusion couple at 850 °C for 100 h.

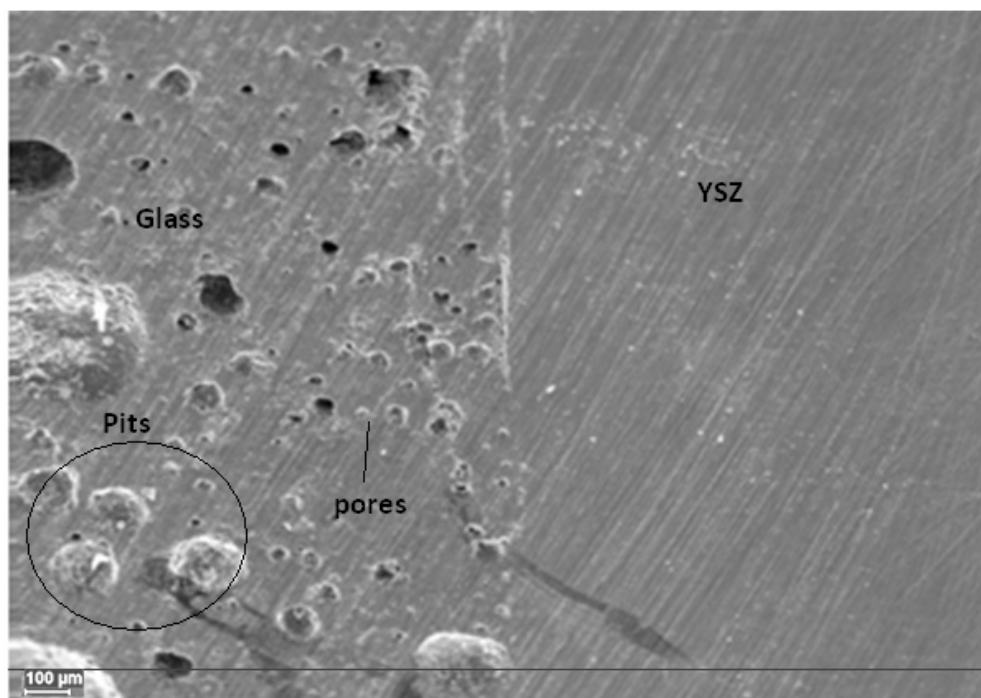


Figure 5.31(a): ML/YSZ glass diffusion couple at 850 °C for 750 h.

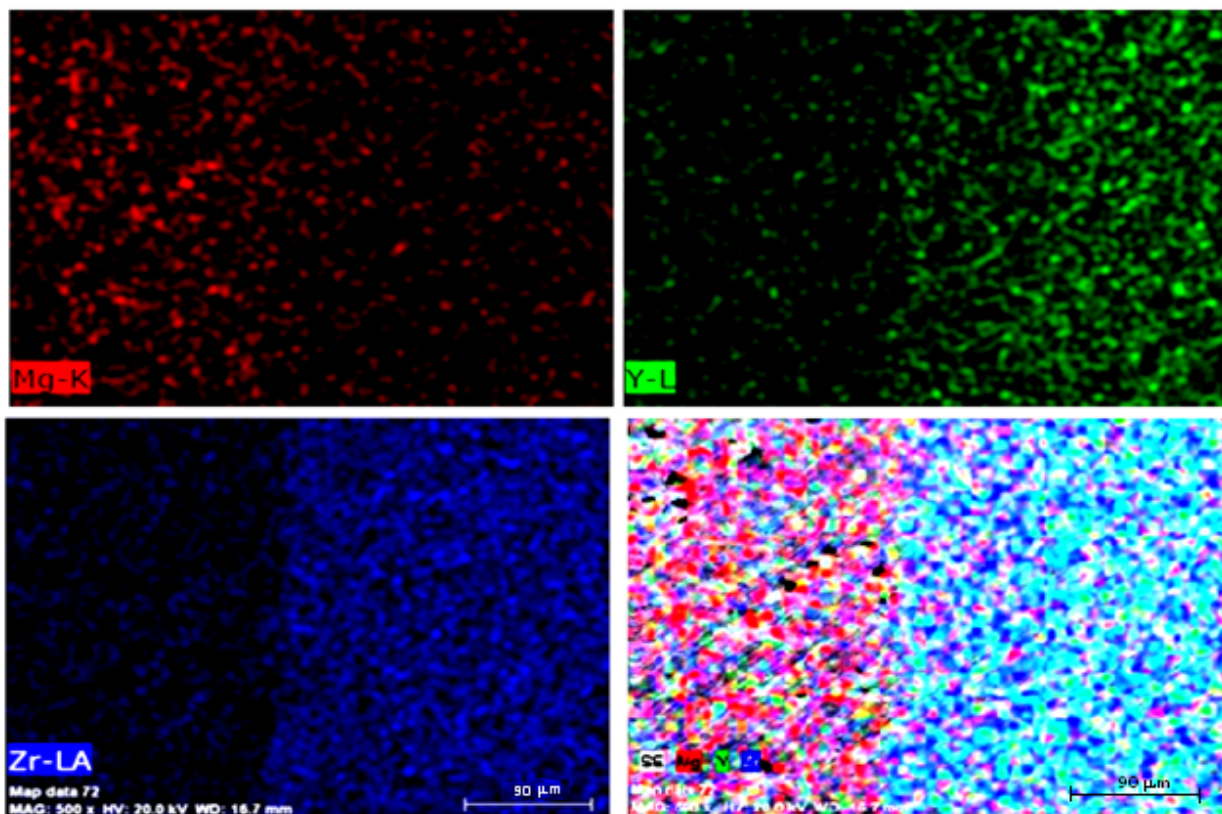


Figure 5.31(b): X-ray dot mapping of ML/YSZ diffusion couple at 850 °C for 750 h.

Even after prolonged heat-treatment of 750 h at 850 °C, the interface of ML/YSZ diffusion couple has shown good adherence (fig. 5.31 (a)). The ML seal has shown good bonding characteristics and absence of delamination. At the same time, the number of pits has increased with heat-treatment duration which could be attributed to volatility of entrapped gases during the process of glass formation. XRD indicated the precipitation of low CTE enstatite (MgSiO_3) phase as shown in fig. 5.8. So, it can be concluded that the ML glass became glass-ceramic after heat-treatment of 750 h. The low CTE of MgSiO_3 must have been responsible for tensile stress, which enhances the pit formation in the glass matrix [54]. From the dot-mapping (fig. 5.31 (b)), it is clear that diffusion of ions has been taken place without any segregation or accumulation at the interface. As the time duration increases from 5 to 750 h, the diffusion of ions decreases for ML/YSZ diffusion couples. This may be explained on account of concentration gradient. Initially, due to large difference of concentration on either side of interface, the diffusion is rapid. But as the concentration equilibrium is attained, the diffusion kinetics gets slow down. In all the diffusion couples, no zirconate or zirconia rich phases have been formed. The results obtained are in well agreement with those obtained from XRD. Higher crystallization has been observed for ML/TBV couple as compared to ML/YSZ couple after 750 h treatment. High degree of crystallization also enhances thermo-mechanical properties of sealants. In addition to this, smoother interfaces have been achieved for ML/TBV couples which could be due to lower CTE mismatch between glass and this electrolyte.

5.5.2 CL/YSZ diffusion couple

Fig. 5.32 (a) shows cross-section of CL/YSZ diffusion couple heat-treated at 850 °C for 5 h. The interface is free from cracks. Very less closed porosity (pits) could be observed in glass which is generally non-problematic as closed porosity is impermeable to gas flow. This closed porosity could be attributed to internal brittleness of glass because of amorphousness after 5 h heat-treatment. Further elemental analysis from dot-mapping (fig. 5.32 (b)) reveals very low diffusion of yttrium and zirconium, whereas calcium has diffused upto greater extent from the glass matrix. The interface is free from any corrosion reaction products as well any segregation. After 100 h treatment at 850 °C (fig. 5.33 (a)), the electrolyte is well adhered with the glass-ceramic.

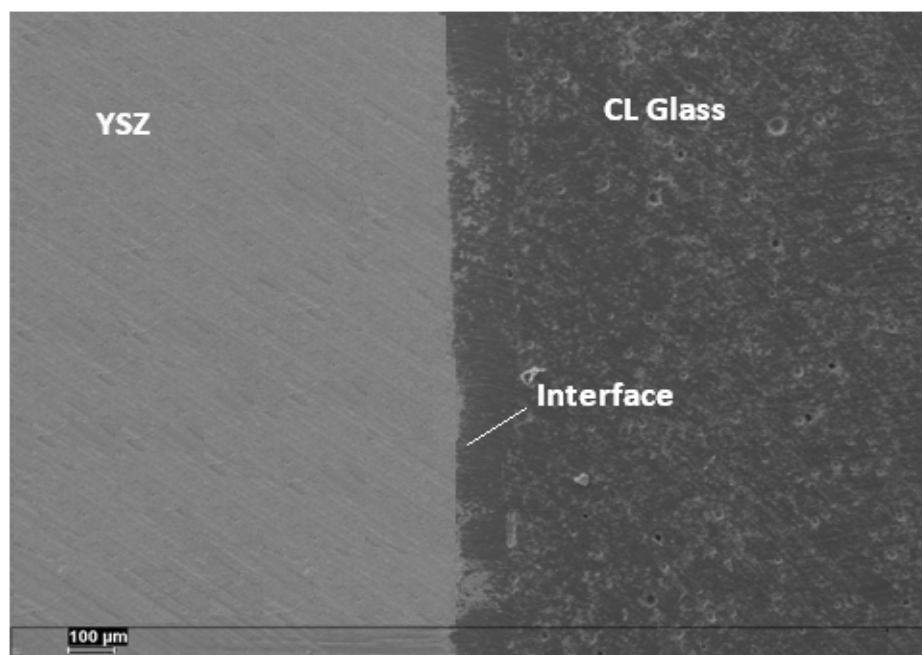


Figure 5.31(a): CL/YSZ diffusion couple at 850 °C for 5 h.

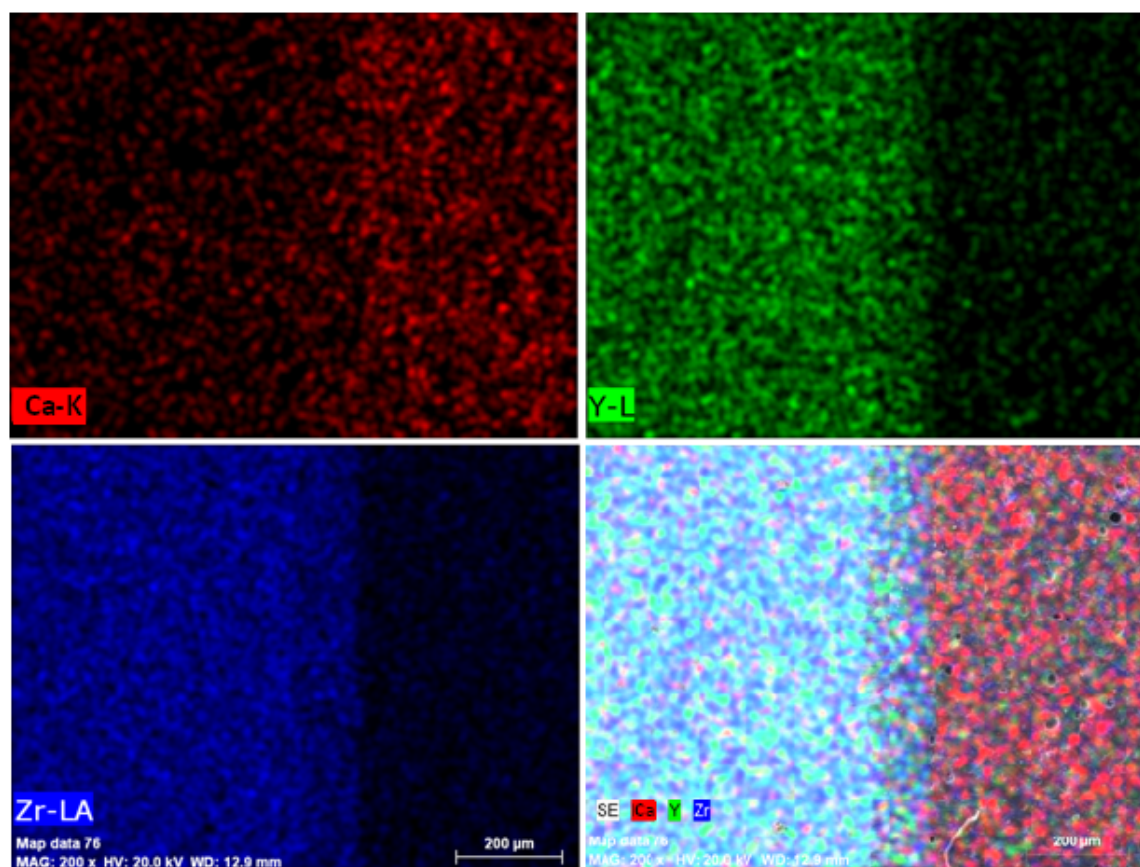


Figure 5.31(b): X-ray dot mapping of CL/YSZ diffusion couple at 850 °C for 5 h.

From the morphological point of view, no structural modifications have been observed at the interface. A strong electrolyte-glass seal bond is observed at the interface without having any detrimental reaction products. The elemental analysis again reveals Z-shaped profile for yttria and zirconia, whereas calcium exhibits S-shape profile (fig. 5.33(b)). The oscillations of yttria and calcium have decreased on either side of interface indicating homogenous diffusion. Prolonged heat-treatment of 750 h at 850 °C has again resulted in good adhesion without any delamination of CL/YSZ interface (fig. 5.34(a)). In addition to this, the sealing region is pore free along with preclusion of undesired reactions or corrosion products. Accumulation of elements could not be seen at the interface even after such a prolonged heat-treatment (fig. 5.34(b)). The diffusion process has also slowed down. This could be due to hinderance in ion transport process provided by crystalline phases formed in glassy matrix [65]. The XRD results validated the presence of CaZrO_3 perovskite structure along with CaZr_4O_9 phase (fig. 5.10). The CTE of CaZrO_3 is $10.4 \times 10^{-6}/^\circ\text{C}$ [66], which is very close to CTE of YSZ. This leads to good thermo-mechanical compatibility between glass and YSZ electrolyte. Figure 5.35 shows the microstructure of YSZ after 750 h treatment. YSZ exhibits average grain size of 212 nm with standard deviation of 1.034. This implies its quite homogenous structure.

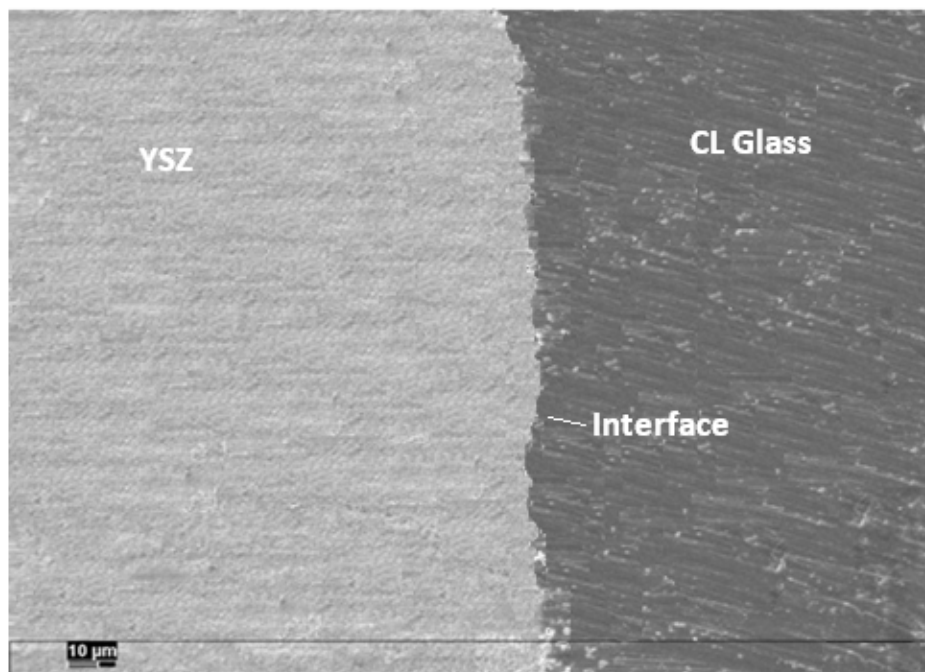


Figure 5.32(a): CL/YSZ diffusion couple at 850 °C for 100 h.

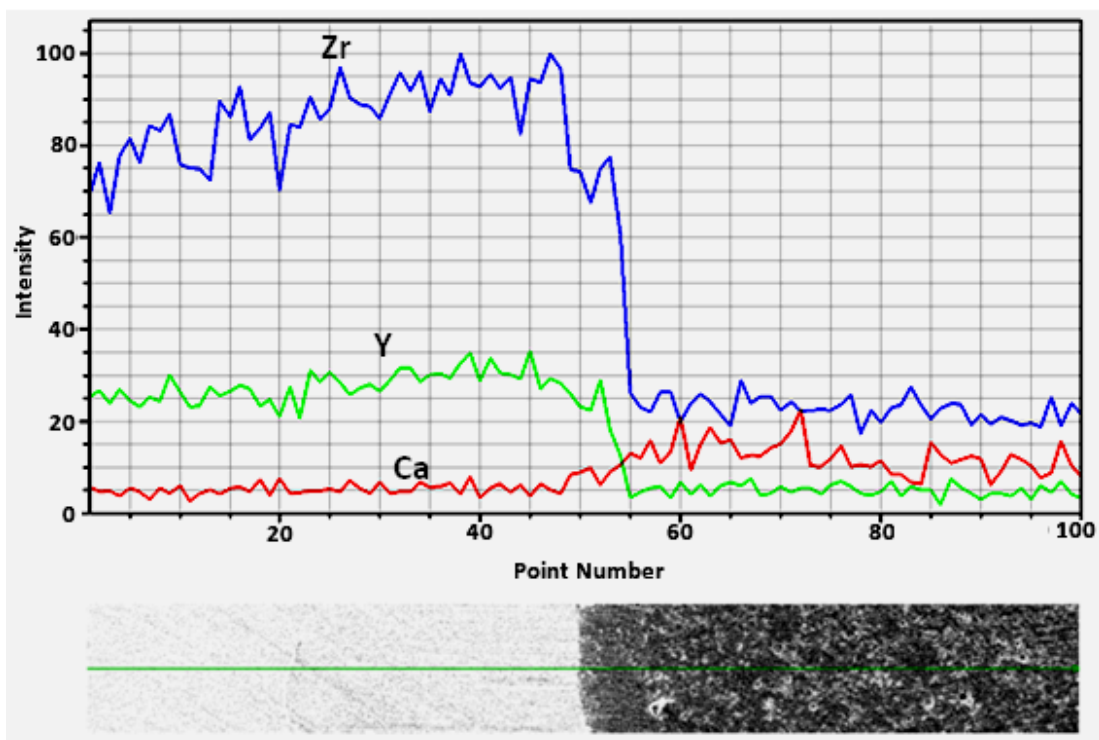


Figure 5.32 (b): X-ray dot mapping of CL/YSZ diffusion couple at 850 °C for 100 h.

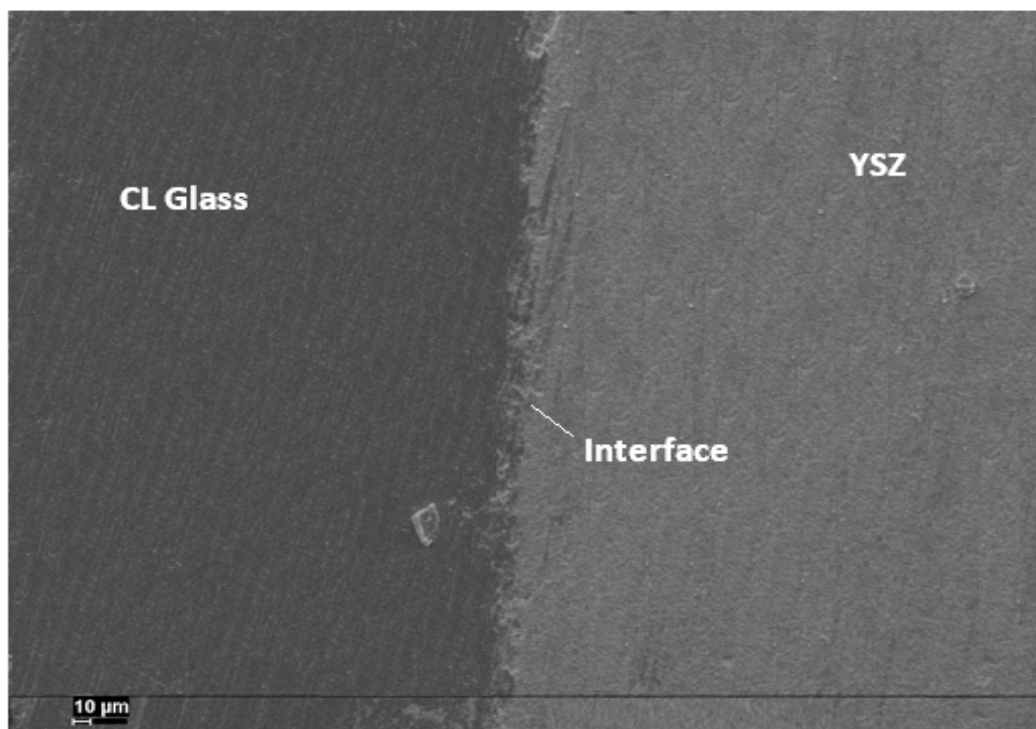


Figure 5.33 (a): CL/YSZ diffusion couple at 850 °C for 750 h.

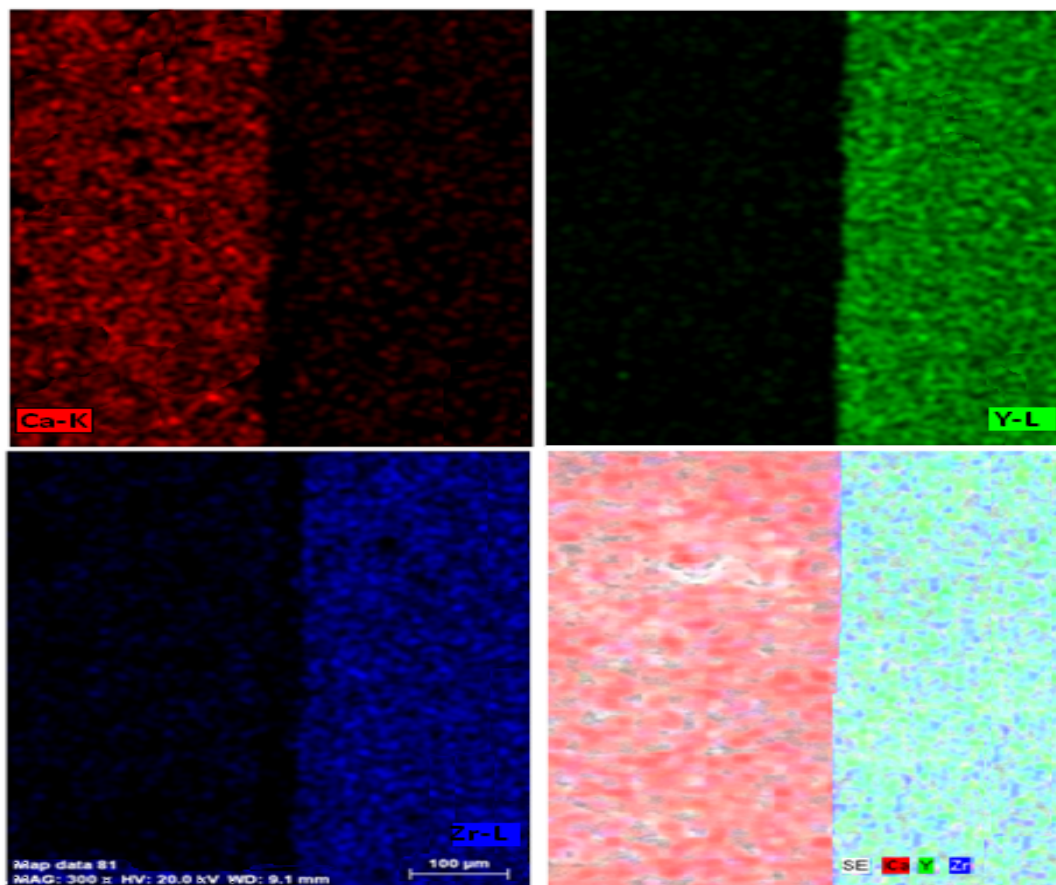


Figure 5.33 (b): X-ray dot mapping of CL/YSZ diffusion couple at 850 °C for 750 h.

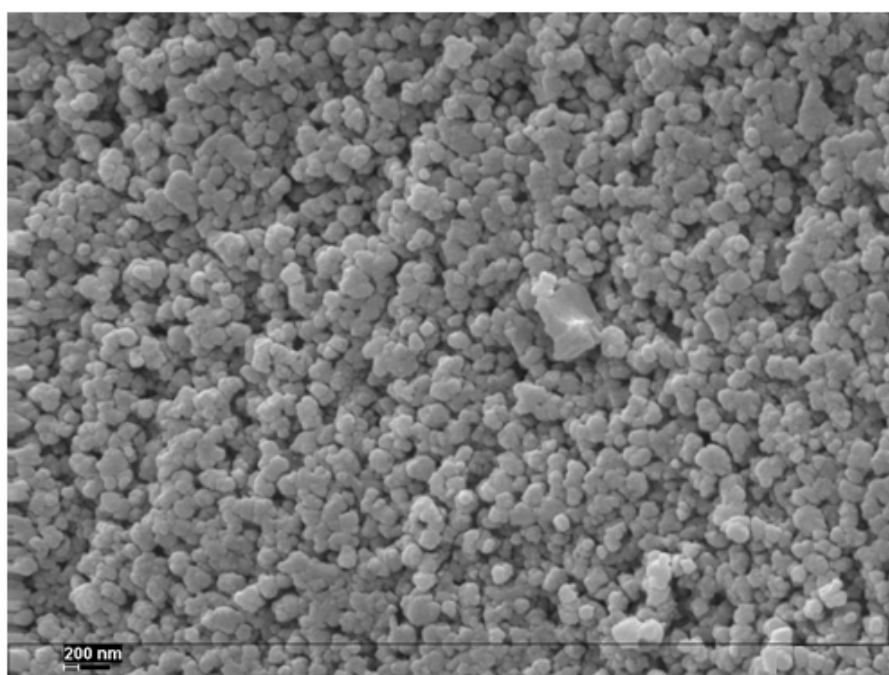


Figure 5.34: Microstructure of YSZ after 750 h heat-treatment at 850 °C.

Hence the chemical durability of joint region is on the higher side even after prolonged durations of heat-treatment. The long-term chemical stability from the point of view of reaction mechanisms involved at interface between glass and YSZ after heat-treatment depicted good bonding characteristics.

5.5.3 SL/YSZ diffusion couple

Fig. 5.35(a) shows cross-section of SL/YSZ diffusion couple heat-treated at 850 °C for 5 h. The absence of cracks at the interface demonstrates good adhesion and structural integrity for the couple. Defect free and very homogenous microstructure is obtained for glass and electrolyte. Delamination could not be observed at the interface. The bonding between glass and electrolyte (YSZ) depicts good bonding characteristics. The elemental analysis from EPMA (fig. 5.35(b)), reveals the highest diffusion of zirconium in 'S' profile. In addition to this, strontium has also diffused out markedly from the glass matrix. The composition spikes show large variation indicating its inhomogeneous distribution.

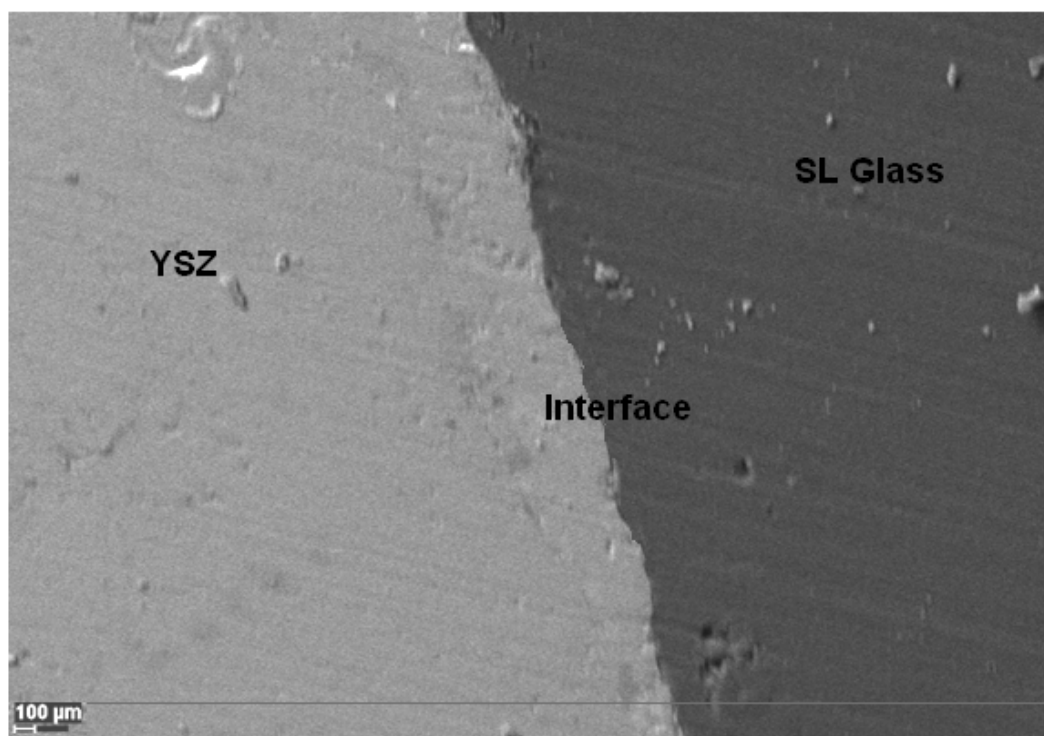


Figure 5.35 (a): SL/YSZ diffusion couple at 850 °C for 5 h.

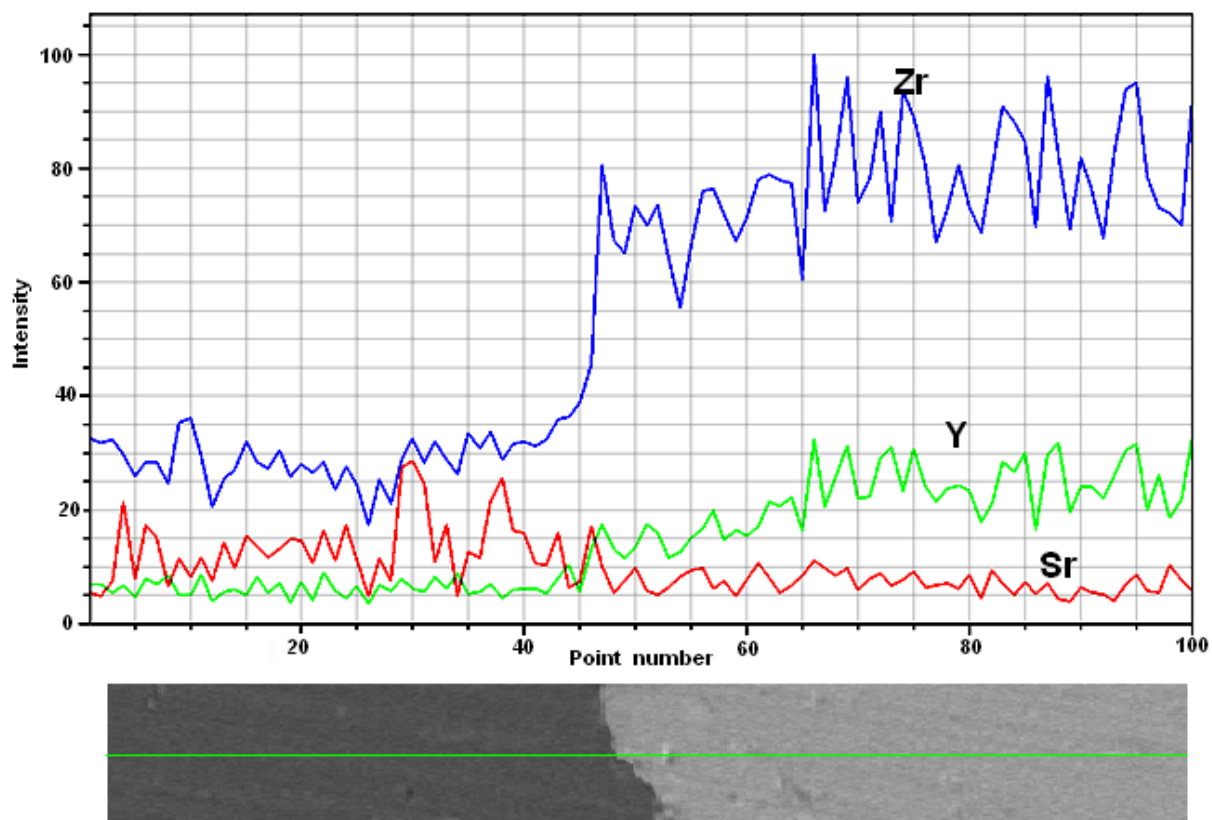


Figure 5.35 (b): EPMA of SL/YSZ diffusion couple at 850 °C for 5 h.

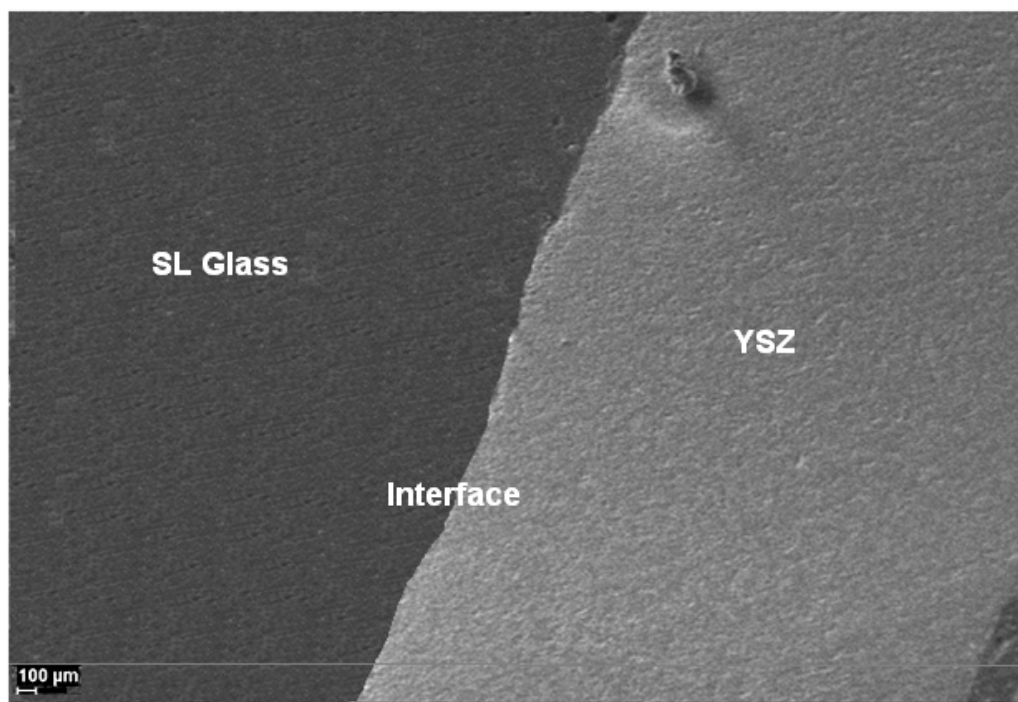


Figure 5.36(a): SL/YSZ diffusion couple at 850 °C for 100 h.

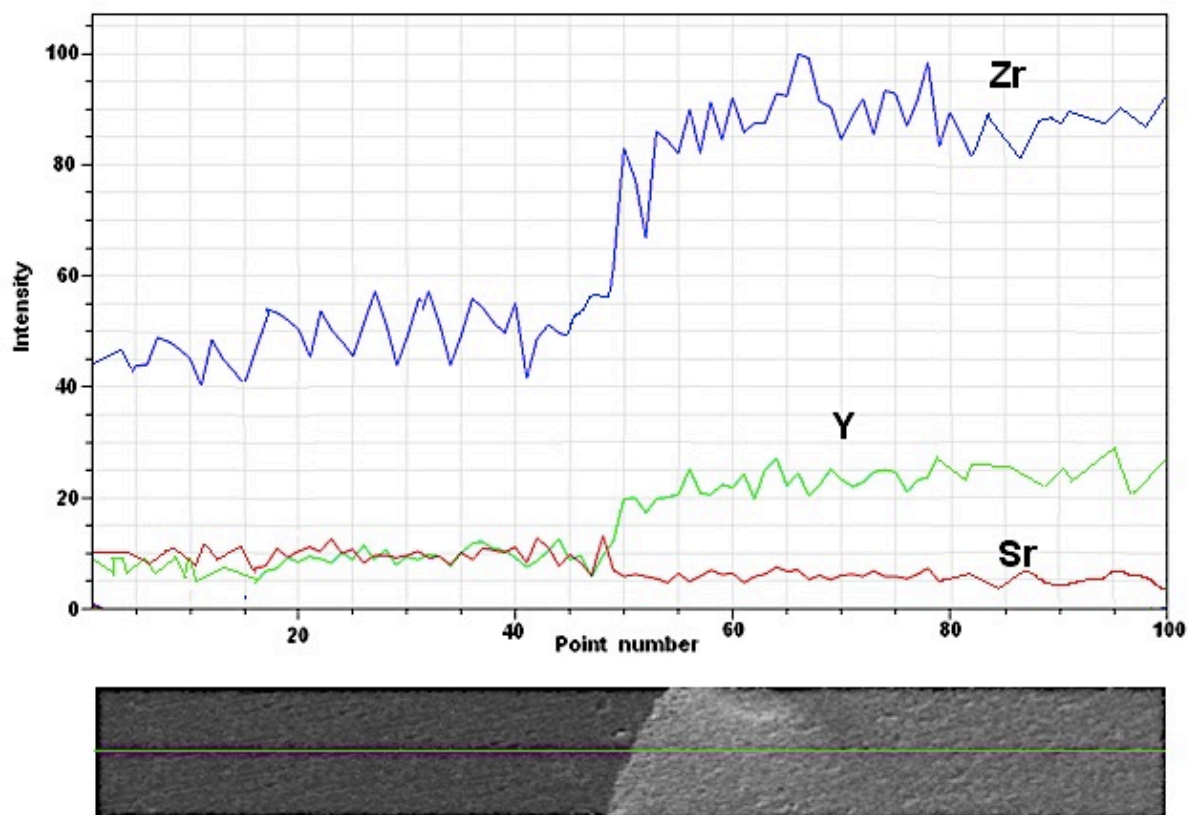


Figure 5.36 (b): EPMA of SL/YSZ diffusion couple at 850 °C for 100 h.

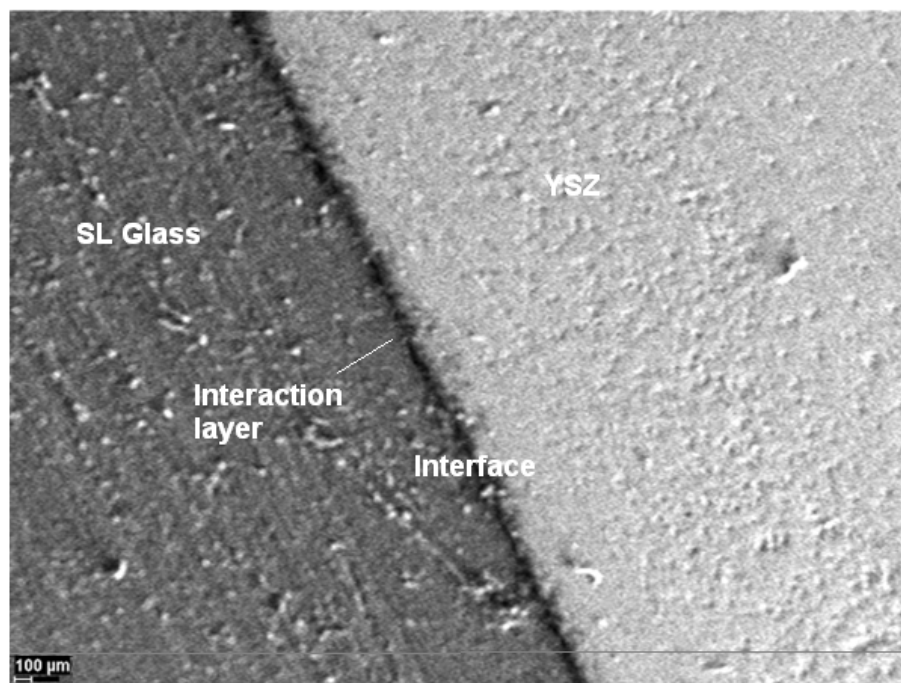


Figure 5.37 (a): SL/YSZ glass diffusion couple at 850 °C for 750 h.

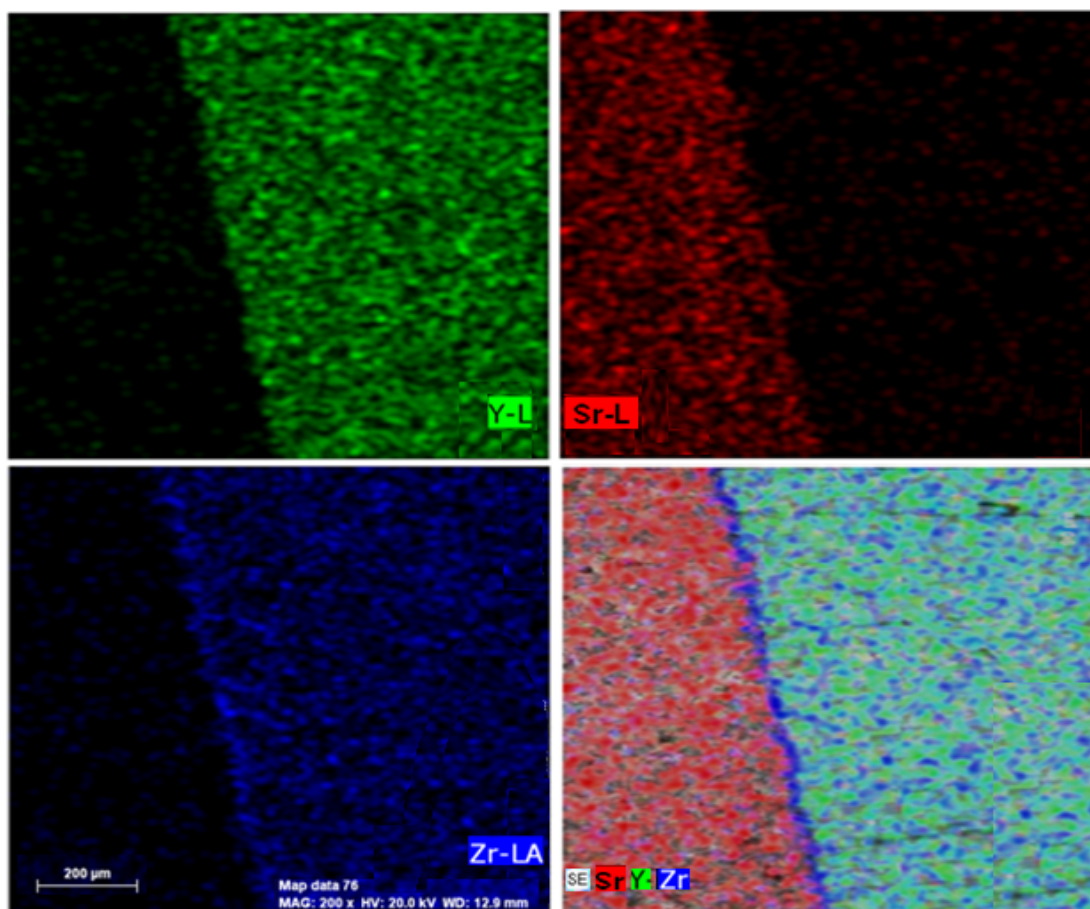


Figure 5.37 (b): X-ray dot mapping of SL/YSZ diffusion couple at 850 °C for 750 h.

No elemental segregation is observed at the interface. After 100 h treatment at 850 °C, very good connectivity between the glass and YSZ is obtained as shown in fig. 5.36(a). The interface and microstructure are very homogenous in nature free from cracks, pores or delamination. The EPMA analysis (fig. 5.36(b)) indicates S-shaped profile for yttrium and zirconium, whereas strontium again diffuses in non-homogenous pattern. The extent of zirconium diffusion has increased after 100 h treatment as compared to its diffusion profile after 5 h. Fluctuations in spectra of elements indicate composition inhomogeneity of glass phase and the formed crystalline phases. Prolonged heat-treatment of 750 h at 850 °C has again resulted in good adhesion without any delamination of SL/YSZ interface (fig. 5.37(a)). After bonding, interaction layer of high zirconium content has been formed at the interface as depicted by dot-mapping and shown in fig. 5.37(b). Zirconium has shown the maximum tendency to migrate and accumulate at the interface. Zirconium concentration becomes noticeable at interface (dark grey layer). The prolonged duration of heat-treatment might have caused significant diffusion of

zirconium. The XRD results validated the presence of SrZrO_3 perovskite structure having CTE of $10.9 \times 10^{-6} / ^\circ\text{C}$ [66], which is very close to CTE of YSZ. This leads to good thermo-mechanical compatibility between the interface of glass and YSZ electrolyte. All the couples of SL glass with YSZ have revealed good bonding and adhesion. Stable zirconate phase has precipitated. No detrimental phase could be observed in all the present samples. Therefore, the SL glass proves to be very desirable sealing for long term SOFC applications.

5.5.4 BL/YSZ diffusion couple

Fig. 5.38(a) shows the interfacial region of BL glass seal and YSZ heat-treated at 850°C for 5 h. No delamination or reaction zone at the interface is seen. At both the edge and inside area, the sealing BL glass ceramic is well bonded to YSZ. Interface in the interior area exhibited porosity of the order of 0.22 mm (area = $37994 \mu\text{m}^2$). The shape of the pores indicates that these have formed due to formation of vapor species. The pits are homogenously distributed in the glass ceramic side. A population of smaller pores is also seen besides larger pits. The cross section of this couple is investigated using X-ray dot mapping (fig. 5.38(b)) in order to detect the possible diffusion of elements from YSZ into the glass sealant. The microstructure within the pit signifies the dendritic crystalline phase embedded in amorphous glassy matrix (fig. 5.39).

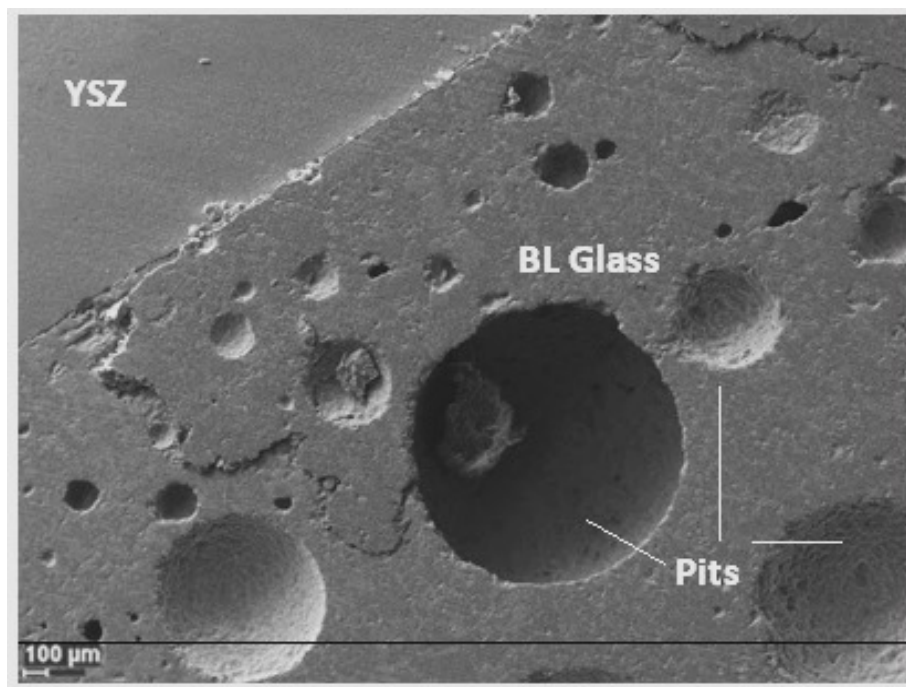


Figure 5.38 (a): BL/YSZ diffusion couple at 850°C for 5 h.

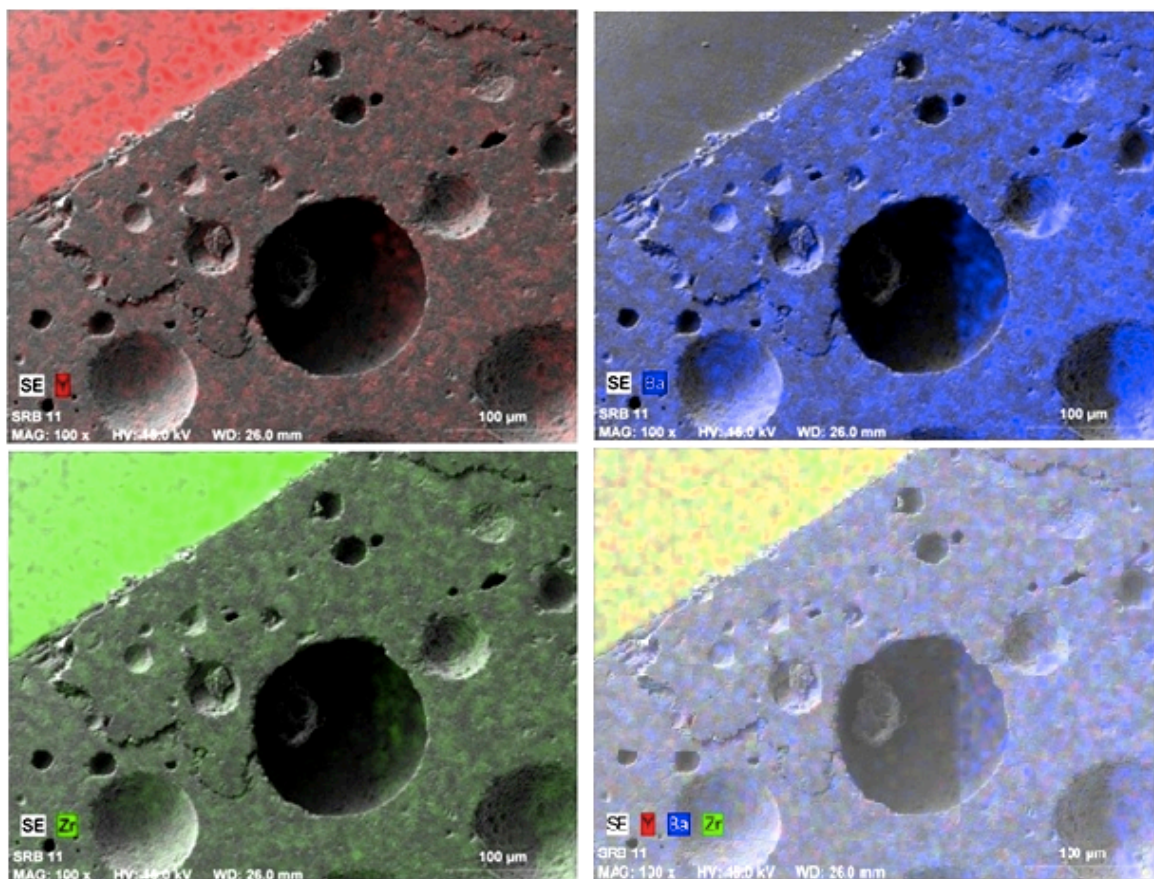


Figure 5.38 (b): X-ray dot mapping of BL/YSZ diffusion couple at 850 °C for 5 h.

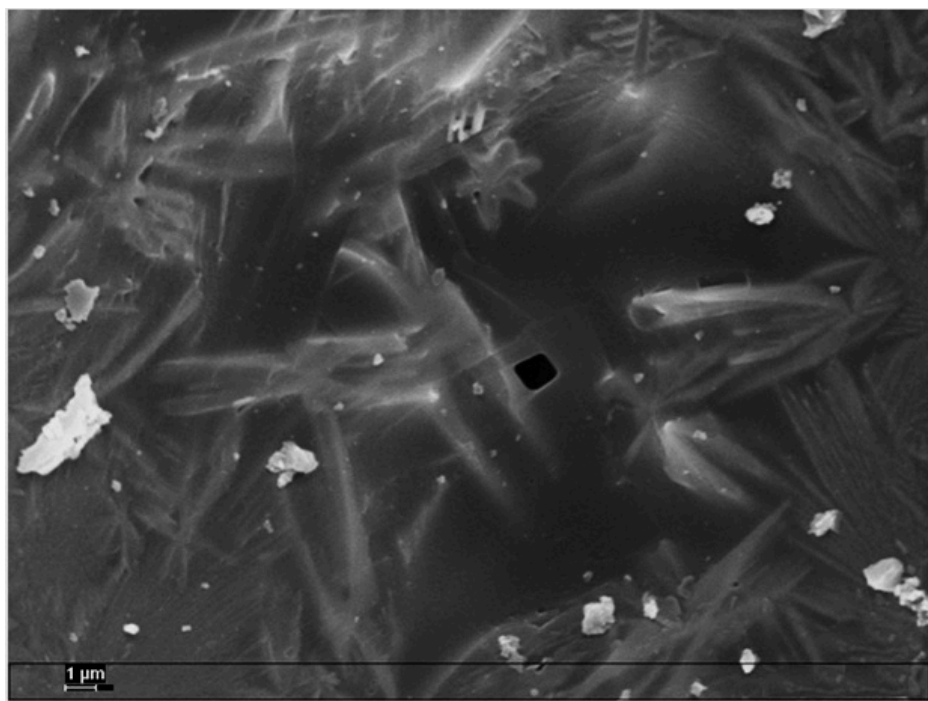


Figure 5.39: Microstructure inside the pit of BL glass.

Dendrites appear when supercooling is large. Generally, dendritic spikes grow, when the temperature gradient is present. Furthermore, it remains isolated as the released latent heat during spike formation raises the temperature of immediate surrounding liquid, hence retarding the growth of other similar projections in its vicinity [67].

For 100 h heat-treated BL/YSZ diffusion couple at 850 °C, the size of closed pits decreased to a size of 0.09 mm (area=25434 μm^2) though the interfacial adhesion is good and free from cracks (fig. 5.40 (a)). The existence of closed porosity (pits) is a usual phenomenon and does not lead to enhancement of leak rate for the final seal [53]. No unusual elemental segregation was identified at glass ceramic surrounding the pores. There was no accumulation of unwanted crystalline phases at the interface as given in elemental analysis (fig. 5.40(b)). The ceramic phases being brittle cannot withstand tensile stresses and therefore lead to crack formation. Fig. 5.41(a) demonstrates the diffusion couple after heat-treatment of 750 h. The pore size subsequently became 0.01 mm (area= 314 μm^2). No separation of interfaces or elemental accumulation is seen in the couple (fig. 5.41 (b)). Therefore, this glass has shown predominantly self-healing behavior with considerable decrease in pore size. Pits can occur due to evolution of dissolved gases or decrease in volume. Sometimes the gases are more soluble in liquid state, than in solid state.

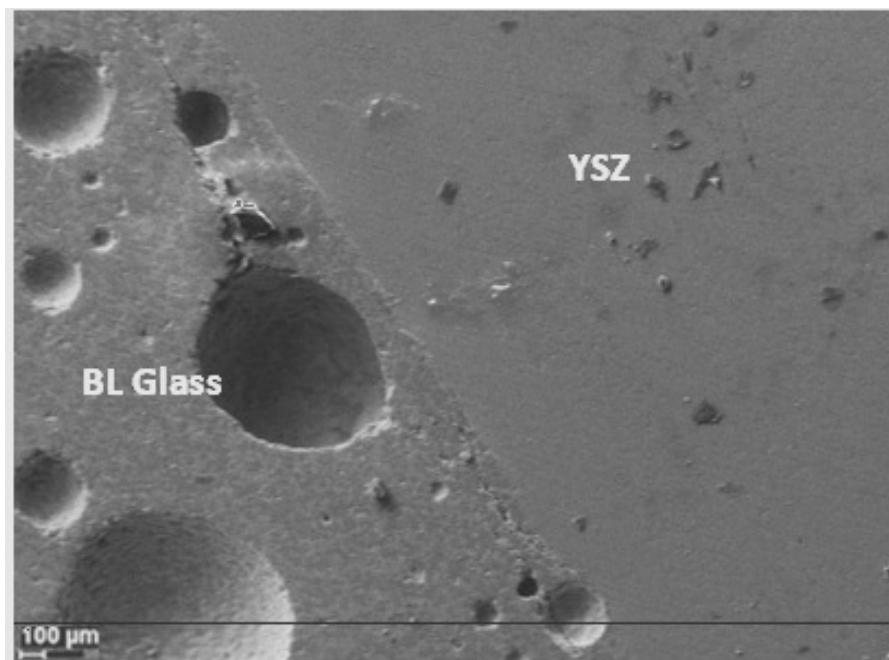


Figure 5.40: (a) BL/YSZ diffusion couple at 850 °C for 100 h.

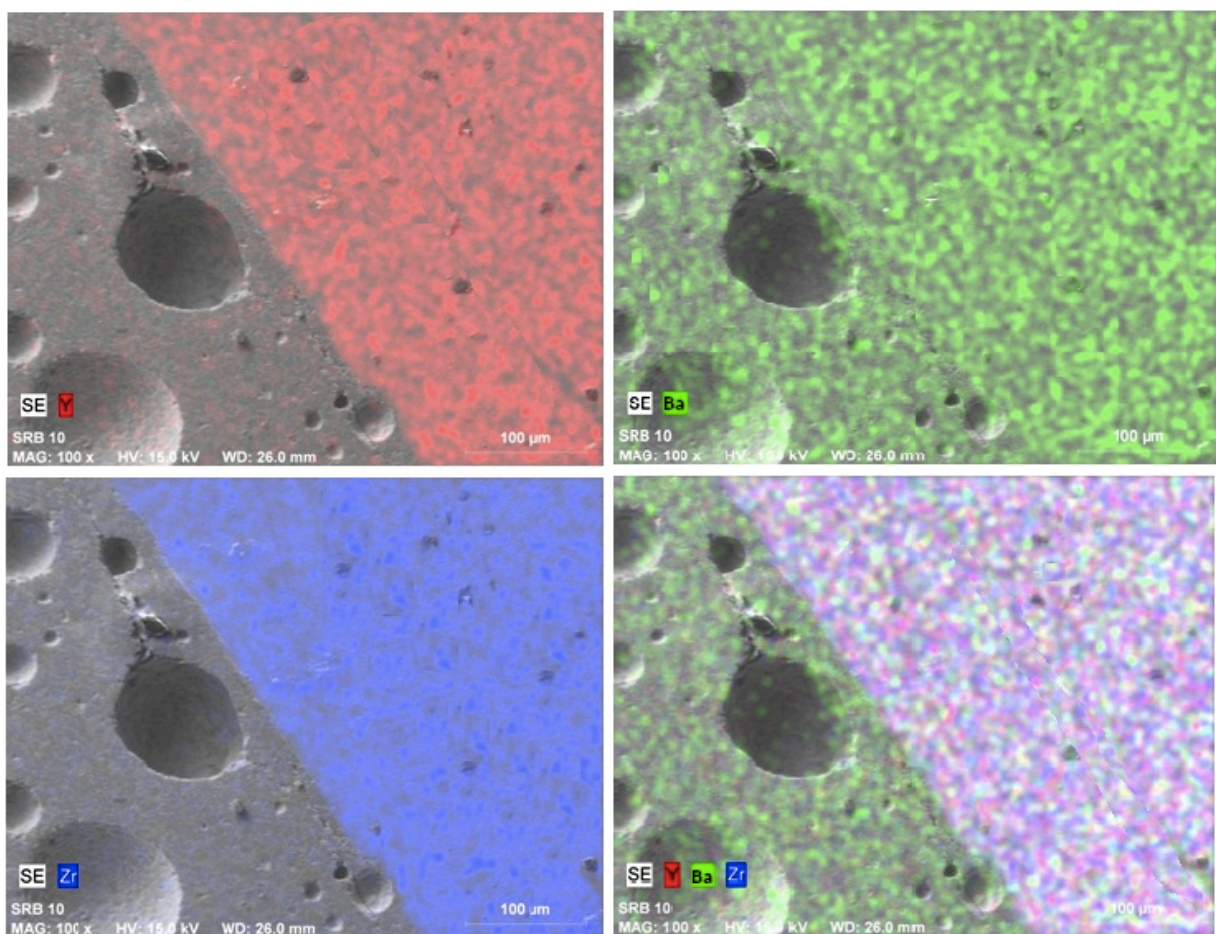


Figure 5.40 (b): X-ray dot mapping of BL/YSZ diffusion couple at 850 °C for 100 h.

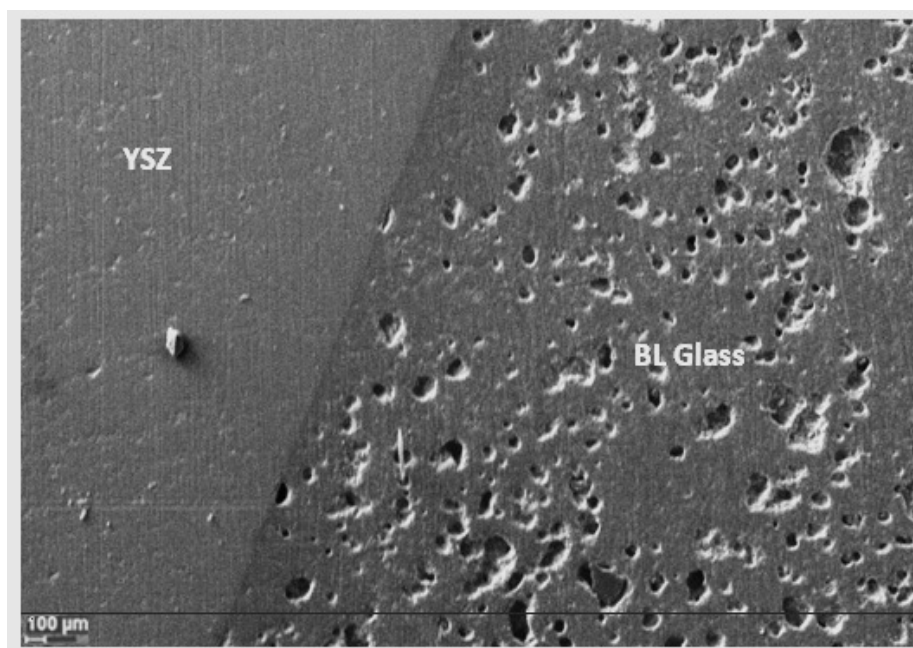


Figure 5.41(a): BL/YSZ diffusion couple at 850 °C for 750 h.

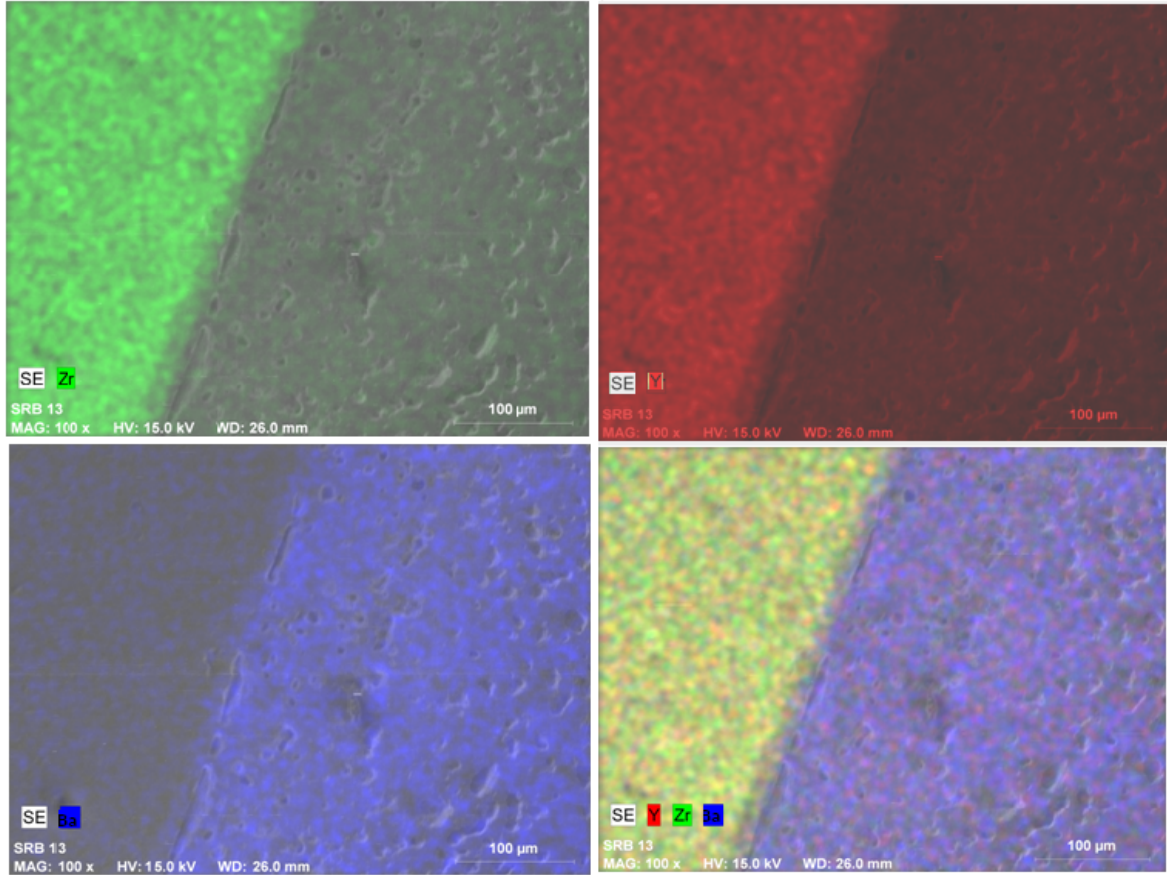


Figure 5.41(b): X-ray dot mapping of BL/YSZ diffusion couple at 850 °C for 750 h.

The solubility of gases, generally, depends upon the applied pressure and temperature. In this case, Sieverts laws hold good for most common diatomic gases such as oxygen, hydrogen and nitrogen etc. [67] :

$$C_g = k\sqrt{p} \quad (5.14)$$

C_g is the solubility of dissolved diatomic gas, k is the constant and p is the pressure of gas. When the dissolved gases are rejected, then they accumulate and may reach a concentration, which causes nucleation of gas bubbles. If the rate of growth of bubbles is much slower than the solid growing around them, then the bubble is trapped inside. The bubbles, which grow under lower hydrostatic head, are larger in size.

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CHAPTER 6

CONCLUSIONS AND FUTURE SCOPE

Overview

The present chapter deals with summary of results obtained from structural, thermal, optical and interaction study of glass/glass ceramics with Crofer 22APU/YSZ/TBV as described in chapter 5. The effect of various modifier oxides on glass structure, activation energy and interfacial kinetics has been compared, concluded and summarized. The interaction behavior of all the diffusion couples have been compared and concluded. At the end the suggestion for future work on the basis of results and discussion obtained in this work is given.

6.1 Conclusions

Replacement of alkaline earth metal modifiers in decreasing field strength order ($ML > CL > SL > BL$) exhibit strong effect on mechanical, structural and band gaps of lanthanum containing borosilicate glasses. With the replacement of higher atomic weight metals like barium in glass, the optical band gap decreases due to increase in number of non-bridging oxygen. The increase in Urbach energy with the replacement of modifier suggests an open structure of the glass due to formation of non-bridging oxygen. In FT-IR spectra, bands are shifted to lower wave number slightly, with the addition of Ba^{2+} in glass due to higher content of NBO's. This data is well supported by Raman spectroscopy and FT-NMR. Similarly, BL glass sample has higher values of optical basicity, refractive index and oxide ion polarizability, which is again manifestation of higher number of NBO's in this glass with lower field strength. Among all the glasses, ML glass showed highest hardness and fracture toughness, which can be attributed to high bond strength of Mg-O.

Glass with higher activation energy possesses lower free volume. BL glass exhibited highest change in linear CTE and highest jump in bulk thermal expansion. In addition to this, higher covalency of glass network leads to low abrupt change in coefficient of bulk thermal expansion (α_f). ML glass has lowest v followed by BL glass, hence exhibiting lowest nucleation sites. Lowest v value and highest E_c for ML implies smaller crystallization tendency in these glasses. A non-integer value of Avrami parameter n indicates the possible occurrence of two crystallization mechanisms. The XRD pattern of coupled glasses could not form any crystalline phases having iron and chromium as constituents even after prolonged heat-treatment of 750 h.

The diffusion couple of all the glasses with Crofer 22APU, (heat-treated at 850 °C for 5, 100 and 750 h) have been investigated. The coupled ML and BL glass sealant has shown high residual porosity in comparison to coupled CL and SL glass sealant. In addition to this, CL and SL glass has almost crystallized upon heat-treatment whereas ML and BL glass possesses some amorphousity. SL and BL glasses exhibit acceptable CTE, which is required for SOFC applications. No Cr-rich zone could be seen along the interface in any of the diffusion couple, indicating absence of any adverse reaction. The crystallization process is slow in BL glass couple as compared to other glasses. SL glass seals have shown high hermeticity and structural integrity with Crofer 22APU even after prolonged heat-treatment. On the other hand, BL glass seal exhibited substantial number of pores after prolonged heat-treatment. The absence of unwanted oxide products in all the diffusion couples confirmed high hermeticity and gas tightness of seals with low embrittlement.

The low temperature electrolyte chosen for interaction study is titanium doped bismuth vanadate. Sample $x = 0.20$ has shown maximum conductivity of $1.2 \times 10^{-3} \text{ S cm}^{-1}$ with minimum activation energy of 0.19 eV at 800 °C in all the studied samples of $\text{Bi}_2\text{V}_{1-x}\text{Ti}_x\text{O}_{5.5-\delta}$ ($0.05 \leq x \leq 0.20$). CTE is also higher for $x = 0.2$ sample indicating higher asymmetric potential well. High conducting γ phase is stabilized for $x = 0.15$ and $x = 0.20$ at room temperatures which is evident from XRD as well as thermal analysis results. All the samples have shown reduction during the cooling cycle indicating that Ti^{3+} must have not oxidized to Ti^{4+} .

Diffusion couples of all the glasses with intermediate temperature (TBV) and high temperature electrolytes (YSZ) as a function of heat-treatment duration revealed good adhesion without the formation of any detrimental reaction products such as cristobalite and cordierite phases at the interface. MgSiO_3 phase has been observed after heat-treatment of 750 h treatment in both the coupled ML/YSZ and ML/TBV seals. Additionally, ordered pyrochlore $\text{La}_2\text{Si}_2\text{O}_7$ phase has been obtained in ML coupled seal after heat-treatment of 750 h at 800 °C. There is complete absence of zirconate phase during the interaction of ML glass with YSZ even after heat-treatment of 750 h. Porosity could be seen in glass matrix for ML/YSZ diffusion couple, which could be due to thermal stresses.

The perovskite zirconate (CaZrO_3) phase is formed during the interaction of CL glass with YSZ after heat-treatment of 100 h. During later stage of heat-treatment, CaZr_4O_9 phase has also formed. In case of CL/TBV diffusion couple, Ca_2SiO_4 orthosilicate phase has been obtained after heat-treatment of 100 h at 800 °C. Its volume fraction increased with increasing heat-treatment duration. CL glass seal has shown better structural integrity, hermeticity and air-tightness with high-temperature electrolyte (YSZ) as compared to low temperature TBV electrolyte. Though in both the cases, no detrimental reaction products are formed at the interface even after 750 h of treatment.

The perovskite zirconate (SrZrO_3) phase emerged out during the interaction of SL glass with YSZ after heat-treatment of 100 h. In case of SL/TBV diffusion couple, $\text{Sr}_3\text{Si}_3\text{O}_9$ and pyrochlore $\text{La}_2\text{Si}_2\text{O}_7$ phases has been obtained in coupled seal after heat-treatment of 100 h at 800 °C. The volume fraction of all these phases has increased after 750 h heat-treatment. No corrosion product could be seen at SL/TBV interface, but delamination and crack formation along the interface is observed after 750 h treatment. SL/YSZ diffusion couples reveal excellent adhesion and bonding characteristics. Noticeable zirconium layer has been formed at the interface after 750 h treatment, yet the hermeticity of gas tight seal is maintained.

The BaSiO₃ phase have been obtained for both the coupled glasses after 750 h treatment. The glass has shown higher devitrification resistance along with controlled crystallization. No zirconate phase formation has been observed in coupled BL/YSZ glass. Interestingly, BL glass has shown self-healing characteristics. In all the diffusion couples, very good bonding characteristics are seen along with complete preclusion of any unwanted elemental segregation. Table 6.1 summarizes the interfaces obtained during present investigation.

Table 6.1: Interfaces formed in coupled seal after heat-treatment for 750 h treatment.

Glass/component 	Crofer 22APU	TBV	YSZ
ML	Pores	Delamination	Smooth
CL	smooth	Very smooth	Very smooth
SL	Smooth (very little porosity)	Small delamination	Very smooth
BL	No delamination but high porosity	Self –healing	Self-healing

Among all glass seals, CL glass showed best and intact interfaces even after prolonged heat-treatment as is clear from table 6.1.

6.2 Future scope

Lanthanum borosilicate glasses have shown quite promising results, yet lot of work remains to be done. These glass sealants have to be tested in real SOFC conditions. The leak rate test measurements of the samples under reducing and oxidizing atmosphere can be further investigated for their long-term evaluation as suitable sealing material for SOFC application. In addition to this, Interaction study between CL glass and other components of SOFC is required for longer durations in oxidizing and reducing atmospheres.