Chapter 1

Introduction

This chapter provides us the structural chemistry of borophosphate glass. The basic principles of the borophosphate glass was get understood by the structural chemistry, which was put forwarded by many experiment in recent years. Chapter also discusses the history of glass, synthesis & structural development of glass and application of borophosphate glass. It also includes the recycling of glass & finally the aim of the work is summarized.

We are going to discuss the following points----

1.1 Natural glass

1.2 History of artificial glass

1.3 Definitions of glass

1.4 Story of glass formation Myth and Legend

1.5 Current Historical Knowledge of glass formation

1.6 Types of glass

1.7 Preparation methods of glass

1.8 Borophosphate glass

1.9 Melt quench technique

1.10 Importance and Applications

1.11 Recycling of glass

1.12 Aim of the Work
1.3 Definitions of glass

This section was composed to give an overview of glass science, including what a glass is and the popular parameters used to characterize it. Glasses have been defined a number of ways by many authors, its definition changing as research progresses and pushes back the boundaries of glass science. A definition by Shelby seems to be the most appropriate: “an amorphous solid completely lacking in long range, periodic atomic structure and exhibiting a region of glass transformation behaviour”.

1.4 Story of Glass Formation Myth and Legend

Where and when glass production began is uncertain. It is thought by some that the first glass was probably developed in the Mitannian or Hurrian region of Mesopotamia, possibly as an extension of the production of glazes (5000 BCE). Around this same time, a new material called faience was developed, which was produced by utilizing a variety of techniques to create a glaze layer over a silica core. It may have been invented in either Sumeria or Egypt, but its full development was accomplished in Egypt, and it is therefore commonly referred to as Egyptian faience. Although this material was used to craft beads during the third and fourth millennia BCE, it involved sintering (fusion below the melting point), rather than the complete melting of the silica mixture. As such, faience can be thought of as an intermediate material between a glaze and glass. Glass as an independent material is not thought to predate 3000 BCE, with the first glass.

1.5 Current Historical Knowledge of glass formation

While the accounts discussed so far make entertaining stories, they are not commonly accepted as historically accurate and currently scholars believe that glass was discovered either as a byproduct of metallurgy or from an evolutionary sequence in the development of ceramic materials. These two hypothetical origins are deemed plausible as both early technologies had procedures that could be considered precursors of glass.
1.6 Types of Glasses:

Depending on the network former used, glasses can be classified as silicate, borosilicate, alumina silicate, borate, phosphate glasses, chalcogenide glasses etc. and depending on its end used as optical glasses, sealing glasses, special application glasses etc.

1.7 Preparation methods of glass

Different techniques have been used to prepare amorphous glassy materials in various forms like bulk, sheet, powder, thin films, etc.

Most of the traditional glasses are inorganic and non-metallic, but currently large number of organic glasses is in front line and they need different preparation techniques. Metallic glasses are also becoming very common with every passing year. Besides the conventional melt-quenched technique, glasses are also prepared by other methods such as physical vapor deposition, thermal evaporation, sputtering, glow discharge, chemical vapor deposition, sol-gel method, applying intense shock waves mechanical alloying etc.

1.8 Borophosphate Glass

Borophosphate glasses have interesting structural network due to the presence of two glass formers B$_2$O$_3$ and P$_2$O$_5$ thus incorporating mixtures borate phosphate and borophosphate units. A range of cations had previously been studied in borophosphate to assess the structure and some glass properties. These includes Li$^+$, Na$^+$, K, Ca$^{2+}$, Ba$^{2+}$ and Zn$^{2+}$. The addition of B$_2$O$_3$ modifies the properties of phosphate glasses by cross-linking phosphate chains to improve chemical durability.

Previous structural studies of Borophosphate glasses indicates that boron atoms form either trigonal B(3), or tetrahedral B(4), sites within the borophosphate glass network depending on composition. The possible borophosphate [analogous to AlPO$_4$ structure] and borates units present in borophosphate structural networks.
1.9 Melt-quenching

Melt-quenching is the oldest method being used for the preparation of glass. An essential pre-requisite for the glass formation from a melt is that, the cooling has to be sufficiently fast to prevent nucleation and crystal growth. Rates of cooling required for glassy phase formation are different for different materials. For example certain glass formers such as B$_2$O$_3$, P$_2$O$_5$ etc. will from glassy phase even under conditions of slow cooling (like 1K/s). Most of the glasses with B$_2$O$_3$, SiO$_2$, and P$_2$O$_5$ etc. as network formers can be prepared by this method. However, for preparing metallic glasses, cooling rates of the order of $10^7$ K/s is required which require special techniques like melt spinning, melt extraction etc.

1.10 Importance and Applications

In all commercially important glasses B$_2$O$_3$ is used as a most common glass former and is also used as a dielectric glass former material. Over a wide range of modifier concentration borate glasses can be formed at relatively lower melting temperature. B$_2$O$_3$ is a basic glass former in borate glasses because it has higher heat of fusion and lower cation size. The most important point of borate glass formation is the structural investigations of boron and related doped system. B$^{3+}$ ions are triangularly co-ordinated by oxygen atoms in borate glasses and triangle units are corner bonded in a random configuration. In identifying several borate groups IR studies and 11B MAS NMR investigation were important. Borates group consists of boron oxygen triangle and tetrahedral which forms the glass network at various modifications levels. Up to 33.3% of Na$_2$O is found in alkali modified borate glasses. Where there is continuous formation of BO$_3$ - BO$_4$ units and further increase in alkali which leads to the reconversion of BO$_4$ - BO$_3$ with non bridging oxygen. Other oxides can enter the glass network as a network former and also as a network modifier. Because of this structure of glass is expected to be different from that of alkali borate glasses. In this study we report the synthesis and structural studies of borophosphate glass.
1.12 Aim of the Work

To study the synthesis and characterization of lithium calcium borophosphate glass doped with TMI is the main aim of this work. This study focused on the synthesis of borophosphate glass with unique concentration pattern. That is melt quench technique. And resultant products are characterized with different characterization technique.

Chapter 2

Experimental

2.1 Introduction

Chapter - II In this chapter first of all we have discuss the preparation of glass, Raw materials used for the glass preparation is shown in table. We have briefly discussed the batch preparation and batch calculations by taking suitable examples. And tables are made accordingly. After calculating tables we have discuss the preparation by a melt quench technique. Over all process is summarized in the flow chart. This flow chart shows procedure of the glass preparation to its characterization.

Characterization of the glass has been done by FT-IR, UV, XRD, Micro hardness, Photoluminescence, Chemical degradation, Refractive Index, Conductance, Density and DSC. This chapter gives the brief information of the methods which are used for characterization.

Glass Preparation

Glasses were prepared by conventional melt quench technique. It involves batch preparation, grinding / mixing, calcinations, melting, quenching and annealing. For effective mixing and reaction among different constituents, the reactants were thoroughly ground in a mixer or aged mortar and subjected to different heating steps depending on the type of glass, prior to final melting and quenching process. During calcinations the nitrates, carbonates, sulphates chlorides etc. of constituent elements transformed into their oxides. Alumina crucibles were used for calcinations and melting purposes.
2.2.1 Batch preparations

The glass composition was weighed according to weight percent to give a 30gm batch as given in Table 2.1 A to I. (Details of glass compositions tried).

The quantity of each constituent was determined for each batch depending on the composition of glass. This was done using the standard formulae of different compounds and their dissociation reactions.

For example, let us consider diammonium hydrogen phosphate and sodium nitrate, which incorporates in glass network as $\text{P}_2\text{O}_5$ and $\text{Na}_2\text{O}$ respectively.

**a) Diammonium hydrogen phosphate (DAP) dissociates at 198°C as follows –**

\[
2(\text{NH}_4)_2\text{HPO}_4 \rightarrow \text{P}_2\text{O}_5 + 2\text{H}_2\text{O} + 4\text{NH}_3 \uparrow + \frac{1}{2} \text{O}_2 \uparrow + \frac{1}{2} \text{H}_2
\]

\[
2(\text{NH}_4)_2\text{HPO}_4 \equiv 1\text{P}_2\text{O}_5
\]

2 [molecular weight of $(\text{NH}_4)_2\text{HPO}_4] \equiv 1 [molecular weight of \text{P}_2\text{O}_5]

2 [131.97 gm of DAP] \equiv 1 [141.94 gm of P$_2$O$_5$]

263.94 gm of DAP \equiv 141.94 gm of P$_2$O$_5$

1.8595 gm of DAP = 1 gm of P$_2$O$_5$

Thus 1.8595 gm of $(\text{NH}_4)_2\text{HPO}_4$ dissociates to form 1 gm P$_2$O$_5$.

**b) Sodium nitrate (NaNO$_3$) dissociates at 306°C as follows –**

\[
2\text{NaNO}_3 \rightarrow \text{Na}_2\text{O} + 2\text{NO}_2 \uparrow + \frac{1}{2} \text{O}_2 \uparrow
\]

\[
2\text{NaNO}_3 \equiv 1 \text{Na}_2\text{O}
\]

2 [molecular weight of NaNO$_3$] \equiv 1 [molecular weight of Na$_2$O]

2 [84.99 gm of NaNO$_3$] \equiv 1 [62 gm of Na$_2$O]

169.98 gm of NaNO$_3$ \equiv 62 gm of Na$_2$O

2.7416 gm of NaNO$_3$ \equiv 1 gm of Na$_2$O

Thus, 2.7416 gm of NaNO$_3$ dissociate to form 1 gm Na$_2$O.

Similarly, the dissociation reactions of different compounds carried out to form 1 gm of their respective oxides.

2.2.2 Batch Calculation

An example of batch calculation may be demonstrated here for
30Na2O – (60-y) B2O3–yP2O5 –10Al2O3  glass system

Where, Y=5 mole%

Glass composition –

Table 2.1--- Glass composition

<table>
<thead>
<tr>
<th></th>
<th>30 Na2O</th>
<th>55 B2O3</th>
<th>5 P2O5</th>
<th>10 Al2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mole %</td>
<td>30</td>
<td>55</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>Mole. Wt.</td>
<td>62</td>
<td>69.62</td>
<td>141.94</td>
<td>101.96</td>
</tr>
<tr>
<td>Wt / mole</td>
<td>18.6</td>
<td>38.291</td>
<td>7.097</td>
<td>10.196</td>
</tr>
</tbody>
</table>

2.2.3 Batch composition

30 gm batch of 30Na2O – 55 B2O3–5P2O5 –10Al2O3 glass system contains quantities of the raw material as – 12.857 gm of Na2CO3, 15.484 gm of B2O3, 5.341 gm of DAP, 30.343 gm of Al (NO3)3 9H2O

Similarly, the quantities of the initial constituents for other systems can also determined

2.2.4 Batch Melting – (Melt-quenching)

The mixed charge was taken in alumina crucible. The 99.9% purity recrystallised alumina crucibles of conical shape were used for melting the mixed charge. The crucible was kept in muffle furnace and the temperature of the furnace was increased gradually. The furnace operates up to 850°C continuously and up to 950°C for 2 hrs. The crucible was heated to attain temperature 900-950°C

2.3 Characterization

The qualitative and quantitative analysis carried out to investigate various physicochemical aspects of the glass samples is described herein. Melt quench technique was used to prepare glass samples. Prepared glass samples of a Borophosphate; Calcium borophosphate; Lithium calcium borophosphate
and doped lithium calcium borophosphate samples of glass were characterized by the following characterization techniques.

Prepared samples were characterized by the following technique---

1. Density
2. Molar Volume
3. R.I.
4. Corrosion
5. Micro hardness
6. Dielectric Constant
7. FTIR
8. U.V.
9. Photoluminescence
10. D.S.C.

Chapter 3

STUDIES OF BOROPHOSPHATE GLASSES

3.1 Introduction

A Borophosphate glass shows different useful properties. So that borophosphate glasses becomes one of the important glass of compounds. We find borate and phosphate in many glass systems. Calcium doped borophosphate found application as low melting glass solders. Several borophosphate glasses exhibit high chemical durability. Keeping in view of the fact that borophosphate glasses have attractive applications chemically more durable compared to both pure phosphate and pure borate glasses. Also borophosphate glasses are promising and diversified optical applications because of their good transparency, low refractive indices, good optical properties, and low dispersion from the ultraviolet to the near infrared regions.

In view of these promising and diversified optical properties, these glasses are considered as materials for optical component such as IR domes, optical filters, modulators memories and laser windows, further these glasses may be considered as good materials for hosting lasing ions such as chromium / rare earth ions these glasses provide a low photon energy environment to minimize non radioactive losses.
3.2 Experimental
Chemically pure i.e. analytical grade chemicals are used. To prepare the glass system, chemicals which are used are of A-1 grade i.e. of analytical grade. Method used for preparation of glass was conventional melt quench technique. Chemicals were taken in a mortar. Where they are thoroughly mixed and grinded for about 30-45 min. 30 gm charged was taken in alumina crucible. This charge contain in alumina crucible, it kept in a muffle furnace for about 4-5 hours. Temperature was ranged up to 900-1000 °C. When these charges attain a desirable viscosity and become homogeneous. Then it was poured on a metal plate. Glass was annealed at 330°C in a annealed furnace. After 2-3 hours we can take it out at room temperature. Resultant glass was characterized by characterization method.

3.3 STUDIES OF BOROPHOSPHATE GLASSES
Glass of the system

\[ 30\text{NaO} - (60-y) \text{B}_2\text{O}_3 - y\text{P}_2\text{O}_5 - 10 \text{Al}_2\text{O}_3 \]

(\(y=5, 10,15,20,25\) and 30 mol. %)

This system was used to prepare glass. It was characterized by measuring their density (\(\rho\)), molar volume (VM), dielectric constant, Refractive Index, Chemical degradation, Microhardness, \textit{Effect of Density on RI}.

3.3.1 Characterization of Borophosphate glass
Glass can be distinguishing from one another by their different physical characteristics. In crime it is good evidence for investigators. They can suspect the scene of crime. Glass is made up of soda, lime, silicon oxide (sand) and other oxides. So, all these materials make glass hard and brittle. Magnesium, calcium, aluminium and sodium are found in most of the window glasses. Glasses used in automobiles are heat resistanance glasses. They are pyrex glasses containing boron oxides. When one surface touches other surface there is a exchange of physical properties Which is known as Locard principle. Physical properties include colour, melting point, density, weight, volume, R.I. and boiling point. We are going to characterize glass sample by these characterization.

\[ 30\text{NaO} - (60-y) \text{B}_2\text{O}_3 - y\text{P}_2\text{O}_5 - 10 \text{Al}_2\text{O}_3 \]
The detailed characterization procedure is given in chapter II.

3.3.2 Results and discussion

3.3.2.1 Density measurements

Different types of glass have different densities. The density and molar volume observed for borophosphate glasses shows that as density increases molar volume also increase. Variation in physical properties with different composition is measured.

3.3.2.2 Refractive Index

Refractive index is important physical property of a glass. It is used to calculate purity, to identify the substance and to measure the concentration. Different glasses have different refractive indexes. Optical system which uses refraction possesses RI. Refractive indexes are used to measure solids like gemstones, glasses, gasses and liquids. We have calculated the RI of prepared glass samples.

3.3.2.3 Effect of Density on RI

Effect of density on RI Temperature, pressure and composition are the factors which affect density of medium. But density of medium can affect the refractive index. Density and RI are generally linear at a fixed wavelength. It is not the condition that they should be linear at same wavelength but generally they are. Here in the table we see the calculated Density and Refractive index how it changes. It shows that increases on addition of P$_2$O$_5$ and addition of B$_2$O$_3$ decreases RI of the glass increases and suddenly RI decreases.

3.3.2.4 Dielectric Constant

A study of the physical properties including spectroscopic, dielectric properties etc., of the glasses is of considerable importance because of the insight it gives into the fundamental process-taking place in them. In fact, the physical properties of the glasses are to a large extent controlled by the structure, composition, and the nature of the bonds of the glasses. The investigation of the changes in the physical properties of
glasses with controlled variation of chemical composition, doping etc., is of considerable interest in the application point of view.

This observation supports the viewpoint that there is an increase of space charge polarization owing to the increasing degree of disorder in the glass network.

3.3.2.5 Chemical degradation (corrosion) studies

Polished samples of the borophosphate glass samples of various compositions

\[30\text{NaO} - (60-y) \text{B}_2\text{O}_3 - y\text{P}_2\text{O}_5 - 10\text{Al}_2\text{O}_3\]

Where \((y=5, 10, 15, 20, 25\) and 30 mol. %)

Were exposed to 10% HCl and 10% NaOH separately at room temperatures for 24, 48 and 72 hrs of exposure. The effect of glass composition and the environment (acidic or alkaline) on the degradation behavior of these glasses was studied and interpreted. The dissolution rate was seen to decrease with increase in sodium oxide content. Thus, it strengthens the structure of the glass. Hence the dissolution rate in 10% HCl and 10% NaOH goes on decreasing with increasing sodium oxide content.

3.3.2.6 Micro hardness studies

Indentation technique is used to measure the microhardness of glass sample. Using Reichert Austria Make Microhardness Tester. Sr. No. 363798 Before measurements, the sample was polished with silica carbide paper. We apply 50 gm load for 10 sec. for indentation. Microhardness value was taken as the average of three values.

Chapter 4

STUDIES OF LITHIUM CALCIUM BOROPHOSPHATE GLASSES

4.1 Introduction

Alkali glasses are one of the important class of glassy materials. Alkali glasses are used as optical material, biomaterial and ionic conductors. Chemical durability of the glasses increases by intermixing of phosphate borate glass networks. During this process temperature required is low. Our study is focused on a structure and properties of lithium calcium borophosphate glasses. Our study was aimed to prepare boron rich glass systems. By taking this particular composition results are quite
different. We studied the role of LiO$_2$ and Na$_2$O they are glass modifier. Network modifier behavior of heavier alkali cations has been studied previously to find different structural role than Na and Li. Phosphate glasses can be prepared at moderately low temperatures which eliminates the difficulties in fabrication of devices. Phosphate glasses have low melting and low softening temperatures when compared with silicate glass systems.

Glasses are the important glassy materials. In this chapter we are going to study the Lithium calcium glasses. Glass of alkaline metal reveals a high solubility. Also Lithium calcium glasses possess aqueous durability comparable to silicate composition. Archimedes method was used to determine density and toluene used as immersion liquid. Other characterizations were carried out.

4.2 Experimental:

Glasses having the following compositions were prepared, using analytical grade compounds as the starting materials following the procedure described in chapter II.

$$x\text{Li}_2\text{O-(30-x)}\text{Na}_2\text{O-15CaO-22.5B}_2\text{O}_3-22.5\text{P}_2\text{O}_5-10\text{Al}_2\text{O}_3$$

$$x=5,10,15,20,25$$

The initial constituents used were of 99.5% purity. Mortar pestle was used to mix and ground the mixture thoroughly. 30 gm of charge was taken in a alumina crucible. The charge was then melted using muffle furnace. The melting temperature was optimized at temperatures 850$^\circ\text{C}$ to 1000$^\circ\text{C}$ for respective composition. The charge was melt for 4 hrs. Under these conditions the melt attain a desirable viscosity for pouring. The pouring was done on a flat metallic plate.

Temperature at which glass kept was annealed temperature. The optimized annealing temperatures were found to be 350$^\circ\text{C}$ - 400$^\circ\text{C}$ and the time to about 4 hrs, for the present series of glass samples. For a lesser annealing temperature and dwell time, cracking of the glass was observed.
4.3 STUDIES OF LITHIUM CALCIUM BOROPHOSPHATE GLASSES

\[ x\text{Li}_2\text{O}-(30-x)\text{Na}_2\text{O}-15\text{CaO}-22.5\text{B}_2\text{O}_3-22.5\text{P}_2\text{O}_5-10\text{Al}_2\text{O}_3 \]

(\(x=5,10,15,20,25\))

The structures and properties of glasses in the mixed glass former (MGF) system

\[ x\text{Li}_2\text{O}-(30-x)\text{Na}_2\text{O}-15\text{CaO}-22.5\text{B}_2\text{O}_3-22.5\text{P}_2\text{O}_5-10\text{Al}_2\text{O}_3 \] have been investigated.

4.3.2 Results & discussion

4.3.2.1 Density measurements and Molar Volume Studies

The composition dependence of the density and calculated molar volumes for the series of \( x\text{Li}_2\text{O}-(30-x)\text{Na}_2\text{O}-15\text{CaO}-22.5\text{B}_2\text{O}_3-22.5\text{P}_2\text{O}_5-10\text{Al}_2\text{O}_3 \) these glasses studied in this work. While the density values increases from 2.06 to 2.16 g/cc and volume decreases from 40.38 to 35.5 g/cc cc with increasing LiO\(_2\) content at the expense of Na\(_2\)O & B\(_2\)O\(_3\) which shows the mixed glass former effect, (MGFE). As we see in the graph 4.2 density decreases from 2.16 to 2.06 and molar volume increases from 35.5 to 40.38 when the mole % of Na\(_2\)O decreases.

4.3.2.2 Refractive Index Studies

Refractive Index of the composition

\[ x\text{Li}_2\text{O}-(30-x)\text{Na}_2\text{O}-15\text{CaO}-22.5\text{B}_2\text{O}_3-22.5\text{P}_2\text{O}_5-10\text{Al}_2\text{O}_3 \]

has been carried out using travelling microscope method. We conclude that addition of CaO shows that RI of glass composition decreases as the molar volume decreases and is inversely proportional to the density of the glass.

4.3.2.4 Dielectric constant Studies

The study of dielectric properties such as dielectric constant, dielectric loss tangent and dielectric loss, over a wide range of frequency and constant temperature. The current investigation is aimed at an understanding the structural aspects of

\[ x\text{Li}_2\text{O}-(30-x)\text{Na}_2\text{O}-15\text{CaO}-22.5\text{B}_2\text{O}_3-22.5\text{P}_2\text{O}_5-10\text{Al}_2\text{O}_3 \]
glasses by studying their dielectric properties. With decreasing frequency, increases the dielectric loss increases dielectric constant value and also increases the dielectric
loss tan $\delta$. With decreasing frequency increases the dielectric loss increases dielectric constant value and also increases the dielectric loss tan. As we observe in the fig no. it shows dielectric constant changes with frequency at constant temperature. These conditions suggest that this glass exhibits dielectric relaxation effect. This is supported by the work of Böttcher and Bordewijk.

4.3.2.5 Chemical Degradation (corrosion) Studies

The chemical durability of glass samples was evaluated from dissolution rate (DR) in 10% HCl and 10% NaOH at room temperature. Polished samples of MA glasses of the nominal composition $x\text{Li}_2\text{O}-(30-x)\text{Na}_2\text{O}-15\text{CaO}-22.5\text{B}_2\text{O}_3-22.5\text{P}_2\text{O}_5-10\text{Al}_2\text{O}_3$ where $X = 5, 10, 15, 20 \& 25$ mole % were exposed for 24, 48 & 72 hrs of exposure. The effect a glass composition and environment (acidic or alkaline) on the degradation behavior of these glasses was studied and interpreted. The route or rates of dissolution are characteristic of the particular cation and the conditions employed. The dissolution rate for these NKABP glasses was seen to be moderately lower than the other; this indicates that due to the addition trivalent cation aluminum, which increase the chemical stability of glasses.

4.3.2.6 Micro hardness Studies

Micro hardness of the glass is studied for following composition

$$x\text{Li}_2\text{O}-(30-x)\text{Na}_2\text{O}-15\text{CaO}-22.5\text{B}_2\text{O}_3-22.5\text{P}_2\text{O}_5-10\text{Al}_2\text{O}_3$$

$(x=5,10,15,20,25)$

Here we are plotting graphs of the doped glass sample and one without doped sample. Shows the hardness increases when mol% of Li$_2$O increases. If hardness decreases when the mol% of Na$_2$O increases in all rest glass samples.

4.3.2.7 FTIR Studies

Infrared (IR) spectroscopy is one of the important techniques which are used to study the local arrangement in inorganic glasses. FTIR analysis of

$$x\text{Li}_2\text{O}-(30-x)\text{Na}_2\text{O}-15\text{CaO}-22.5\text{B}_2\text{O}_3-22.5\text{P}_2\text{O}_5-10\text{Al}_2\text{O}_3$$

Infrared absorption spectra of glasses in the Calcium Sodium Borate System are shown in Fig spectroscopy gives good correlations between the essential features and the structural data and it is useful technique for the identification of different types of
linkages among the glasses. IR spectroscopy has been proven to be a useful tool for investigating the structure and dynamics of amorphous solids. The structural units built around the glass former cations can be evidenced by vibrational spectroscopy. Each spectrum for all investigated glasses contains the number of bands at approximately the same wave numbers. Therefore, one may conclude that the large content of CaO open up the network and force BO$_4$ units to interconnect with the B-O-B, resulting in IR spectrum with sharp peaks. In sodium calcium borate glasses peaks in the regions 600-800 cm$^{-1}$ are assigned to the vibration of the cation (Ca) in the network, to the boroxol [BO$_3$] and the formation of [BO$_4$], Peaks in the region 800-1200 are due to dibroate, pentaborate and the metaborate. The peaks observed in the region 1200-1750 cm$^{-1}$ are due to pentaborate, arise from B-O stretching vibration of [BO$_3$]$^3-$ & the intense one is due to the metaborate chain.

4.3.2.8 U.V. Studies

The Lithium calcium borophosphate glasses have been characterized with UV-visible spectrophotometer and it has shown interesting results.

Transmission characteristics for different glass composition having different thickness are shown in Fig. Transmission in the range 300-800 nm is found to be 45-65% in these glasses. The optical study with UV-visible spectroscopy, transmission in the range 300-800 nm is found be 60 to 85% in these glasses.

The optical transmission spectra of glasses containing mixed alkali show a sharp UV cutoff at 350 to 365 nm for all these glasses. The UV spectra of mixed alkali dependent upon the glass compositions originate from different points of ordinates.

4.3.2.9 X-ray diffraction study

Powder X-ray diffraction patterns of all the borosilicate glass samples showed broad peaks, characteristic of glass structure. Representative XRD pattern is shown in Fig, which confirms the amorphous nature of the investigated glass samples.

Powder X-ray diffraction patterns of all the samples showed a broad peak which confirms the formation of glass.
4.3.2.10 DSC Study

Using Differential Scanning Calorimetric DSC measurements gives us the qualitative and quantitative results about chemical and physical changes which involve change in heat capacity or exothermic or endothermic changes. Fig 4.12 shows the amorphous nature of the glass sample. Fig. 4.13 shows the increased amorphous fraction. As temperature goes on increase the amorphous nature an increase. However on continuous heating, next step of amorphous material is to become crystalline. When it becomes crystalline it becomes ordered. Our graph shows the same behavior. Fig: 4.13 of shows the heat capacity is increases up to 600°C. Small exothermic peak is observed between 90-100°C. Study shows the parallal observations of Greer A.L.

Chapter 5

STUDIES OF LITHIUM CALCIUM BOROPHOSPHATE GLASSES DOPED WITH TRANSITION METAL ION

5.1 Introduction

Boro-phosphate glasses containing transition metal oxides are of special interest. Hence, some sodium- Boro-phosphate glasses containing Co, Ni & Cr (TMI) were prepared and investigated. The structural investigation indicated the presence of dierent borate groups as well as tetragonal phosphate units. The obtained density and the calculated molar volume values showed approximately linear increase. The increase of the density can be attributed to the divergences in the molecular weights. Usually, phosphate glasses are of little interest due to their low chemical durability and high moisture absorbance. But the addition of boron oxide to the phosphorous oxide during melting produces boro-phosphate glass which appears to be of high technological and scientific interest. Moreover, the introduction of selected transition metal ions to the glass network appeared to be very helpful for investigating the glass structure as well as to improve the physical properties of the glass, mainly those properties which are related to electronic movement within amorphous solids. The importance of the prepared glasses is due to their valuable uses in the _fields of magnetic and semiconducting materials.

.5.2 Experimental Work
The composition of the prepared glasses was selected via the criteria that they have the following molecular formula:

\[ \text{20Li}_2\text{O-10Na}_2\text{O-15CaO-}\left(\frac{22.5-y}{2}\right)\text{B}_2\text{O}_3-\left(\frac{22.5-y}{2}\right)\text{P}_2\text{O}_5-10\text{Al}_2\text{O}_3 - y\text{Cr} \]

\( (Y=0.5, 1.0, 1.5, 2.0) \)

Chemically pure oxides were used to prepare the glass batches. The obtained batches, after complete mixing, were melted in porcelain crucibles using an electrically heated furnace for 3-4 hrs at 1000 °C. The melts were stirred several times to ensure that the obtained glasses are well homogenized. Then the melts were quenched by pouring onto a pre-cooled stainless-steel plate, and after sitting they were directly transferred to the annealing furnace at 300 °C. The glass samples were left for 6 hours in the annealing furnace to obtain strain free samples.

5.3 STUDIES OF LITHIUM CALCIUM BOROPHOSPHATE GLASSES DOPED WITH Cr (TMI)

The prepared glass samples were cut and the polished with Si- Carbide paper with various grade (80, 120, 250, 300, 400 & 600) and kerosene.

5.3.2 Results and discussion

The color change in Chromium doped borate glasses has been reported. Greenish colored glass samples are obtained, the change in color has been attributed due to the structural rearrangement of cobalt ions

5.3.2.1 Density

The density \( d \) of all samples were measured via Archimedes method, using toluene as an immersing liquid of stable density [0.866 g/cm3]. The specific volume \( V_s \) of a sample was then calculated as the inverse of the obtained density value. In the investigated mixed alkali glass samples, the observed decrease in density and increase in molar volume with mole % of Cr glass network become continuously close packed up to this level of doping. This is in agreement with reported literature.

5.3.2.2 R.I.

R.I. of the preferred glass sample is obtained by the using travelling microscope method. Formula used for it is
R.I. $\frac{zDx}{zy}$

Where: $z$ = Final reading

$x$ = Initial reading

$y$ = Sample reading

Graph and the values from the observation table shows that as addition of $B_2O_3$ and $P_2O_5$ decrease the R.I. increases. Meanwhile here the addition of Cr (TMI) increases.

**5.3.2.4 XRD pattern**

All measurements were performed on finely ground samples, which were analyzed by X-ray powder diffraction. The phase formation is checked by the normal scan (1.0 degree/m) in the range of $10^0$-$80^0$. The XRD measurements were performed at room temperature in air. In X-ray diffraction spectra, no peaks have been observed, which confirms the amorphous nature of the samples of the present glass system. All the samples are shown to be single phase and the X-ray diffractions patterns of sample. This indicated that all the glasses studied are in pure amorphous and non-crystalline phase.

**5.3.2.5 Dielectric constant**

Investigations on dielectric properties of transition metal ion doped glasses help to throw some light on insulating/conducting character of the material. Investigations on the spectroscopic properties such as such as optical absorption and electron spin resonance can be used as probes to identify the valence states and the environments of the dopant ions in the host glass network. Infrared and Raman spectral studies throw light on the structural aspects of the glasses. The study of dielectric properties, such as dielectric constant, dielectric loss tangent and dielectric loss over a wide range of frequency and constant temperature.
5.3.2.6 Chemical Degradation

The result of the corrosion test for the polished samples of TMI glasses were carried out in 10% NaOH and 10% HCl solutions at room temperature for 24 hrs to 96 hrs of exposure. The dissolution rate was seen to be higher in acidic medium as compared to alkaline medium. In 10% HCl solution, the rate of dissolution of for glass Cr 0.5, Cr 1.0, Cr 1.5 i.e. \(20\text{Li}_2\text{O}-10\text{Na}_2\text{O}-15\text{CaO}-\left(22.5-y/2\right)\text{B}_2\text{O}_3-\left(22.5-y/2\right)\text{P}_2\text{O}_5-10\text{Al}_2\text{O}_3 - y\text{Cr}\) is maximum.

5.3.2.7 Microhardness

Microhardness of the borophosphate glass is studied for following composition

\[20\text{Li}_2\text{O}-10\text{Na}_2\text{O}-15\text{CaO}-\left(22.5-y/2\right)\text{B}_2\text{O}_3-\left(22.5-y/2\right)\text{P}_2\text{O}_5-10\text{Al}_2\text{O}_3 - y\text{Cr}\]

\((Y=0.5, 1.0, 1.5, 2.0)\)

Extra pure glass samples can only show the correct hardness of the glass sample. Which is very rare and in typical condition of glass forming can make it. Following chart shows the hardness in HV. Three readings are taken and average is mentioned in next column.

In all rest glass samples hardness increases on addition of mol% of the TMI.

5.3.2.8 U.V. Studies

The glasses with composition

\[20\text{Li}_2\text{O}-10\text{Na}_2\text{O}-15\text{CaO}-\left(22.5-y/2\right)\text{B}_2\text{O}_3-\left(22.5-y/2\right)\text{P}_2\text{O}_5-10\text{Al}_2\text{O}_3 - y\text{Cr}\]

\((Y=0.5, 1.0, 1.5, 2.0)\)

TMI doping has been characterized with UV – visible spectrophotometer and it has shown interesting results. Optical transmission of the investigated glasses in the UV-visible region of the spectrum was measured and recorded in the range 290-900 nm using a computerized recording spectrophotometer type (Perkin Elmer \(\lambda\)- 950). The experimental results obtained were recorded in the form of % of transmission as a function of wavelength in nm reveals the transmission spectrum of the base sodium borate glass containing various composition of chromium oxide.
These bands are expected to be due to the presence of chromium ions. It is generally accepted the Cr$^{2+}$ ions are absolutely stable in oxide glasses and occur as octahedral and/or tetrahedral coordination depending on the glass composition and condition of melting the glass. The colour of the glasses studied was green in colour.

The observed band at 290-900 nm seen to indicate the presence of Cr$^{2+}$ in the base Lithium Calcium Borophosphate glass. This is in complete agreement with the observed UV-spectra.

5.3.2.9 I.R

Infrared spectroscopy is known to provide insights into the interaction between alkali metal ions and borate glass network. Absorption of these borate glasses is very high in the region of interest of wave number <2000 nm. The FT-IR spectra of 20Li$_2$O-10Na$_2$O-15CaO-(22.5-$y$/2)B$_2$O$_3$-(22.5-$y$/2)P$_2$O$_5$-10Al$_2$O$_3$ – $y$Cr glasses were recorded in the region 450 – 3450 nm & presented in Fig. In the infrared spectral region, the vibration modes of the borate network have three regions.

5.3.2.10 Photoluminescence

It was known that photoluminescence phenomenon was observed in Cr doped with Lithium Calcium Borophosphate glasses. In this study, we report the effect of sintering on photoluminescence. The main emission wavelength of all samples was in a range from 350 nm to 650 nm. This was measured by photoluminescence spectrometer and the change of the fluorescence was due to the alteration of crystal structure of doped TMI.

5.3.2.11 Differential Scanning Calorimetry (DSC)

Where glass transition has no latent heat associated with it. Fig. 5.17 shows the heat flow Vs temperature for a glass. From graph we conclude that heat capacity is increased and molecules become more mobile. Means they are in a state where have more energy. The material is still amorphous and undergo transition from lower energy state to higher energy state. The glass transition temperature (TG) is the temperature at which material undergo a glass transition. As seen in Figure 5.18 the Tg is assigned to the midpoint temperature of the range of temperature during the transition.
Future Scope

Glass is the key material of coming century. We cannot make the things better without glass. Our aim is to support and help the producer to make it more and more better. We developed the borophosphate glass and doped glasses. Our comparison is to show that how borophosphate glass is more convenient for manufacture and durability. Many researcher works on phosphate, borate, silicate etc. glasses.

We purposely chose borophosphate glass. Because of two glass former its strength and durability increases. Also the addition of TMI increases its durability. We have thoroughly characterized it and put forward the result. This helps for the future research. One can make use of it and build more convenient and biodegradable instruments.