Studies of Borate Glasses Doped with Transition Metal Ion (Fe, Cu and TiO$_2$)

1.1 Introduction

Recent technological applications have generated more interest in the studies of different types of glasses. In the recent developments of novel compositions [1-6] of superior physical and chemical properties such as high thermal expansion coefficients [7], low melting and softening temperatures and high ultra-violet and far infrared transmission [8,9], make these glasses potential candidates for many technologically applications, such as sealing materials, medical use [10], and solid state electrolytes [11]. Also because of their unusually high chemical durability and low processing temperature, iron phosphate glass are being considered for vitrifying certain nuclear wastes that are poorly suited for borosilicate glasses [12,13]. Phosphate glasses are also becoming important in optical technology such as in high energy laser application [11], fiber and optical lenses [14, 15]. The relationship between the structure of the host glass and the properties of the doped ions is useful for designing the glasses for different applications.

Transition metals ions (TMI) doped borate glasses have many applications in microelectronics, optical glasses and solid state laser [16-18]. Phosphate glasses containing transition metal oxides (TMO) are of continuing interest because of their applicability in memory switching, electrical threshold, and optical switching devices, etc [19-21].

Glasses with high TiO$_2$ content are of great interest in basic research and technologic applications because of their optical properties and good chemical resistance [22]. Also, the titanate glasses are interesting for obtaining of glass-ceramics with crystalline phases of barium and lead titanates, which present good dielectric properties, by techniques such as quenching and heat treatment [23, 24] or glass irradiated by laser pulse [25]. The main problem is the production of stable glasses, since it is well known that TiO$_2$ into glasses increases spontaneous crystallization tendency during the cooling [26], however, it is reported that additions of glass modifiers and formers SiO$_2$ and B$_2$O$_3$ [27], Al$_2$O$_3$ and Na$_2$O [28], B$_2$O$_3$, K$_2$O, Cs$_2$O and
BaO \[^{[29]}\], PbO and P\(_2\)O\(_5\) \[^{[30]}\], etc., into the glassy network, stabilizes it against bulk or superficial crystallization.

On one hand, glass ceramics based on titanate glasses, containing crystalline phases of K\(_2\)Ti\(_6\)O\(_{13}\) \[^{[31]}\], and/or perovskites of BaTiO\(_3\) \[^{[32]}\], are very promising in structural and electronic applications. The crystals of K\(_2\)Ti\(_6\)O\(_{13}\) have a fibrous tunnel-like structure and exhibit high thermal insulation, mechanical and chemical resistance \[^{[33]}\]. Potassium hexatitanate whiskers are used as reinforcing agent for plastics and metallic alloys because of their price ranges from one-tenth to one-twentieth of the cost of SiC whiskers \[^{[34]}\]. On the other hand, BaTiO\(_3\) is used most extensively in manufacturing of ceramic capacitors because of its high dielectric properties \[^{[35]}\]. Vitrification and crystallization processes of titanate glasses, using melting-casting technique have been studied in a few systems, such as K\(_2\)O-TiO\(_2\) \[^{[36]}\], K\(_2\)O-Al\(_2\)O\(_3\)-TiO\(_2\) \[^{[37]}\] and BaO-PbO-TiO\(_2\)-B\(_2\)O\(_3\)-Al\(_2\)O\(_3\) \[^{[38]}\].

However, the aim of the present study was to investigate the effect of transition metal ion Fe, Cu and TiO\(_2\) concentration on optical properties and the glass forming characteristics of mixed alkali borophosphate glasses. Glasses of the general composition 15Li\(_2\)O – 15Na\(_2\)O – 37.5B\(_2\)O\(_3\) – 25P\(_2\)O\(_5\) – (7.5 –x) ZnO – xTMI, with different concentration of Fe, Cu, TiO\(_2\) were prepared by conventional melt-quench method.

1.2 Experimental

Borate Glasses doped with Transition Metal Ion glasses having the following compositions were prepared, using analytical grade compounds as the starting materials following the procedure described in chapter 2.
<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Glass Code</th>
<th>Composition</th>
<th>Mole % (x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>V</td>
<td>15Li₂O – 15Na₂O – 37.5 B₂O₃ – 25 P₂O₅ – (7.5 –x)ZnO –xFe</td>
<td>X=0.5, 1.0, 1.5, 2.0, 2.5.</td>
</tr>
<tr>
<td>2</td>
<td>VI</td>
<td>15Li₂O – 15Na₂O – 37.5 B₂O₃ – 25 P₂O₅ – (7.5 –x)ZnO –xCu</td>
<td>X=0.5, 1.0, 1.5, 2.0, 2.5.</td>
</tr>
<tr>
<td>3</td>
<td>VII</td>
<td>15Li₂O – 15Na₂O – 37.5 B₂O₃ – 25 P₂O₅ – (7.5 –x)ZnO –xTiO₂</td>
<td>X= 1, 1.5, 2.0, 2.5, 3.</td>
</tr>
</tbody>
</table>

The initial constituents used were of 99.5% purity. These chemicals were thoroughly mixed and ground for 30-40 min in a mortar pestle. The charge (30gm) was calcined in an alumina crucible by considering the decomposition temperatures of their initial compounds.

The calcined charge was then melted using muffle furnace. The melting temperature was optimized at temperatures 900°C to 1100°C for respective composition. The charge was melt for 2-3 hrs. Under these conditions the melt was thoroughly homogenized and attained desirable viscosity for pouring. The pouring was done on a flat metallic plate.

The glass was then annealed at appropriate temperatures. The optimized annealing temperatures were found to be 350°C - 400°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 Mixed Alkali Borophosphate Glass Doped with Fe

\[15\text{Li}_2\text{O} - 15\text{Na}_2\text{O} - 37.5 \text{ B}_2\text{O}_3 - 25 \text{ P}_2\text{O}_5 - (7.5 - x) \text{ ZnO} - x\text{Fe}\]

The structures and properties of glasses in the mixed alkali (MA) borophosphate glass doped with Fe system i.e. 15Li$_2$O – 15Na$_2$O – 37.5 B$_2$O$_3$ – 25 P$_2$O$_5$ – (7.5 –x) ZnO -xFe have been investigated.

Photographs of investigated mixed alkali borophosphate glasses doped with Fe

4.3.1 Characterization

\[15\text{Li}_2\text{O} - 15\text{Na}_2\text{O} - 37.5 \text{ B}_2\text{O}_3 - 25 \text{ P}_2\text{O}_5 - (7.5 - x) \text{ ZnO} - x\text{Fe}\]

The detailed characterization procedure of density, molar volume, X-ray diffraction, UV transmission, infrared absorption spectra, TGA-DTA, dielectric properties, conductivity, micro hardness, refractive index and chemical degradation studies are given in chapter 2.

4.3.2 Results and Discussion

4.3.2.1 Density Measurements

The calculated values of density ($\rho$) and molar volume ($V_m$) for all the mixed alkali borophosphate glasses doped with Fe samples under the investigation have been displayed in table 4.3.1. Variation of density ($\rho$) and molar volume ($V_m$) with Fe mole% for all glass samples is shown in fig. 4.3.1.
Table 4.3.1. Variation in physical properties with composition $15\text{Li}_2\text{O} – 15\text{Na}_2\text{O} – 37.5\text{B}_2\text{O}_3 – 25\text{P}_2\text{O}_5 – (7.5 –x)\text{ZnO} –x\text{Fe}$

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Glass Code</th>
<th>Glass composition (Mol %)</th>
<th>Molar Mass (gm)</th>
<th>Density (g/cm$^3$)</th>
<th>Molar Volume (cc/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Li$_2$O</td>
<td>Na$_2$O</td>
<td>B$_2$O$_3$</td>
<td>P$_2$O$_5$</td>
<td>ZnO</td>
</tr>
<tr>
<td>1</td>
<td>V-1</td>
<td>15</td>
<td>15</td>
<td>37.5</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>V-2</td>
<td>15</td>
<td>15</td>
<td>37.5</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>V-3</td>
<td>15</td>
<td>15</td>
<td>37.5</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>V-4</td>
<td>15</td>
<td>15</td>
<td>37.5</td>
<td>25</td>
</tr>
<tr>
<td>5</td>
<td>V-5</td>
<td>15</td>
<td>15</td>
<td>37.5</td>
<td>25</td>
</tr>
</tbody>
</table>

The density of glass decreases from 1.98 to 1.70 g/cm$^3$ and molar volume increases from 41.07 to 47.53 cc/mol. It may be due to the smaller atomic weight of the Fe samples as compared to the other samples in the system. The molar mass of the samples decreases with increasing Fe composition as shown in figure 4.3.1.

The molar volume increases with increasing Fe composition, it indicate that replacement of B$_2$O$_3$ by Fe increasing the molar volume causing shrinkage of the glass network resulting decreases the density. It means that decreasing molecular weight of oxide ions used in the glass, replacing B$_2$O$_3$ by Fe might be expected decrease the density of these glasses.

The decrease of the modifier contents i.e. Fe acts as glass modifier in the pure B$_2$O$_3$ results in the initial formation of four co-ordinated boron atoms where increased modifier contents induce the formation of non-bridging oxygen containing borate triangles.

This phenomenon is widely known as the ‘boron anomaly’. The increase in density observed is attributed to increase in the rigidity of glass. In general the density of glass system is explained in terms of between the masses and sizes of the various structural units present in glass. In other words, the density is related to how tightly the ions or ionic groups are packed closely in the structure. From fig. 4.3.1 it is observed that the density decreases gradually with increase in Fe content in the
present glass system. The relationship between density and glass composition \((x)\) can be explained in terms of an apparent volume \(V_m\) occupied by 1 gm of oxygen. In this case it is observed that molar volume increases monotonically with increase of Fe content which indicates that the topology of the network is significantly changed with composition.

![Graph showing Variation of density and molar volume with mol% of Fe ion](image)

**Fig.4.3.1. Variation of density and molar volume with mol% of Fe ion**

### 4.3.2.2 XRD Analysis

Powder X-ray diffraction patterns of all the mixed alkali borophosphate glasses doped with Fe (TMI) \((15\text{Li}_2\text{O} – 15\text{Na}_2\text{O} – 37.5 \text{B}_2\text{O}_3 – 25 \text{P}_2\text{O}_5 – (7.5 –x) \text{ZnO} – x\text{Fe})\) glass samples showed broad peaks characteristics of glass structure. Representative XRD pattern is shown in fig. 4.3.2. It confirms the amorphous nature of the investigated glass samples.
Fig.4.3.2. XRD pattern of a mixed alkali borophosphate glasses doped with $x=1.5\%$ of Fe sample.

4.3.2.3 Infrared Transmission

The IR spectra of the mixed alkali borophosphate glasses doped with Fe $(15\text{Li}_2\text{O} - 15\text{Na}_2\text{O} - 37.5 \text{B}_2\text{O}_3 - 25 \text{P}_2\text{O}_5 - (7.5 -x) \text{ZnO} -x\text{Fe})$ glass samples are shown in fig. 4.3.3 and fig. 4.3.4.

Fig.4.3.3. IR spectra of the mixed alkali borophosphate glasses doped with $x=0.5\%$ Fe.
Fig. 4.3.4. IR spectra of the mixed alkali borophosphate glasses doped with $x=2.0\%$ Fe.

Table 4.3.2. IR peaks and their assignments for mixed alkali borophosphate glasses

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Wave No.</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>650 – 1500 cm$^{-1}$</td>
<td>Vibrational modes observed are mainly due to the phosphate network which appears in the range</td>
</tr>
<tr>
<td>2</td>
<td>650 – 900 cm$^{-1}$</td>
<td>Characteristic of the vibrations of bridging P-O-P groups</td>
</tr>
<tr>
<td>3</td>
<td>900 – 1156.88 cm$^{-1}$</td>
<td>Characteristic of terminal P-O and PO$_3$ groups</td>
</tr>
<tr>
<td>4</td>
<td>1156.88 to 1500 cm$^{-1}$</td>
<td>Characteristic of vibrations of non bridging PO$_2$ groups</td>
</tr>
<tr>
<td>5</td>
<td>1341 cm$^{-1}$ and 1741 cm$^{-1}$</td>
<td>B$_2$ and B$_4$ additional sharp peaks</td>
</tr>
</tbody>
</table>

The absorption bands of the mixed alkali borophosphate glasses doped with Fe (15Li$_2$O – 15Na$_2$O – 37.5 B$_2$O$_3$ – 25 P$_2$O$_5$ – (7.5 – $x$) ZnO - $x$Fe) glass samples were good agreement with reported literature$^{[39]}$.  

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4.3.2.4 UV- Visible Spectroscopy

Transmission characteristics for different glass composition having different thickness are shown in fig. 4.3.5. Transmission in the range 300-800 nm is found to be 45-65% in these glasses.

Figure 4.3.5 reveals the variation of transmittance spectra of mixed alkali borophosphate glasses doped with Fe. It can be observed that UV cut off point increases with increasing doping of Fe ions and these values are listed in table 4.3.3.

**Fig.4.3.5. UV spectra of mixed alkali borophosphate glasses doped with Fe ion**

**Table.4.3.3. Band gap of different mixed alkali borophosphate glasses doped with Fe ion.**

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Sample Code</th>
<th>Composition X mole %</th>
<th>% T</th>
<th>UV cut off (nm)</th>
<th>Band Gap in eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>V-1</td>
<td>0.5</td>
<td>213.36</td>
<td>359.28</td>
<td>3.46</td>
</tr>
<tr>
<td>2</td>
<td>V-2</td>
<td>1.0</td>
<td>0.6144</td>
<td>374.83</td>
<td>3.31</td>
</tr>
<tr>
<td>3</td>
<td>V-3</td>
<td>1.5</td>
<td>13.59</td>
<td>434.54</td>
<td>2.85</td>
</tr>
<tr>
<td>4</td>
<td>V-4</td>
<td>2.0</td>
<td>0.523</td>
<td>438.26</td>
<td>2.83</td>
</tr>
</tbody>
</table>
The energy band gap of mixed alkali borophosphate glasses doped with Fe samples decreases with increasing Fe %. This can be attributed to the structural changes that are taking place with introduction of transition metal ions.

### 4.3.2.5 TGA – DTA Analysis

The characteristic temperatures of the obtained glass were determined by thermal gravimetric analysis (TGA) and differential thermal analysis (DTA). The TGA-DTA curves that were obtained for the as quenched glasses (powder) corresponding to the compositions \(x=0.5\%\), 1.0\%, 1.5\% and 2.0\% of Fe content are shown in figs. 4.3.6, 4.3.7, 4.3.8 and 4.3.9, respectively.

![TGA-DTA curve](image)

**Fig.4.3.6.** TGA-DTA curve and characteristic temperature determined for the compositions \(x=0.5\%\) of Fe glass at heating rate of 40°C/min.
Fig. 4.3.7. TGA-DTA curve and characteristic temperature determined for the compositions $x=1.0\%$ of Fe glass at heating rate of 40$^\circ$C/min.

Fig. 4.3.8. TGA-DTA curve and characteristic temperature determined for the compositions $x=1.5\%$ of Fe glass at heating rate of 40$^\circ$C/min.
The glass transition temperatures (T_g) and crystallization temperature (T_c) of the various 15Li_2O – 15Na_2O – 37.5 B_2O_3 – 25 P_2O_5 – (7.5 – x) ZnO -xFe glass samples are listed in Table 4.3.3.

**Table 4.3.4 Transition temperatures of mixed alkali borophosphate glasses doped with Fe system indicated by TGA - DTA curves.**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Glass code</th>
<th>Mole % Fe</th>
<th>T_g (°C)</th>
<th>T_c (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>V-1</td>
<td>0.5</td>
<td>438.18</td>
<td>508.84</td>
</tr>
<tr>
<td>2</td>
<td>V-2</td>
<td>1.0</td>
<td>442.99</td>
<td>516.38</td>
</tr>
<tr>
<td>3</td>
<td>V-3</td>
<td>1.5</td>
<td>442.62</td>
<td>512.04</td>
</tr>
<tr>
<td>4</td>
<td>V-4</td>
<td>2.0</td>
<td>447.88</td>
<td>512.38</td>
</tr>
</tbody>
</table>

From Table 4.3.4 it indicates for higher mol % Fe glass transition temperature (T_g) increases drastically but at lower mol % effect is less because of realignment of network structure. However, the crystallization temperature (T_c) increases with
increasing Fe content of the mixed alkali borophosphate glasses doped with Fe samples. It means that larger changes in glass structure occur.

4.3.2.6 Microhardness

The microhardness of $15\text{Li}_2\text{O} - 15\text{Na}_2\text{O} - 37.5 \text{B}_2\text{O}_3 - 25 \text{P}_2\text{O}_5 - (7.5 - x) \text{ZnO} - x\text{Fe}$ glasses is 2.5203 GPa for 0.5%, 3.6874 GPa for 1.5% and 3.5010 GPa for 2.0% of Fe. From these values indicates the formation of more rigid structure.

The Vickers indentation image of $15\text{Li}_2\text{O} - 15\text{Na}_2\text{O} - 37.5 \text{B}_2\text{O}_3 - 25 \text{P}_2\text{O}_5 - (7.5 - x) \text{ZnO} - x\text{Fe}$ glasses for 0.5%, 1.5% and 2.0% of Fe content are shown in figs. 4.3.10.

![Vickers indentation image of 15Li2O – 15Na2O – 37.5 B2O3 – 25 P2O5 – (7.5 – x) ZnO –xFe glasses for 0.5% of Fe](image)

**Fig. 4.3.10 Vickers indentation image of 15Li2O – 15Na2O – 37.5 B2O3 – 25 P2O5 – (7.5 –x) ZnO –xFe glasses for 0.5% of Fe**

The Vickers indentation image of $15\text{Li}_2\text{O} - 15\text{Na}_2\text{O} - 37.5 \text{B}_2\text{O}_3 - 25 \text{P}_2\text{O}_5 - (7.5 - x) \text{ZnO} - x\text{Fe}$ glasses for 1.5% of Fe content is shown in fig. 4.3.11.
Fig. 4.3.11. Vickers indentation image of 15Li$_2$O – 15Na$_2$O – 37.5 B$_2$O$_3$ – 25 P$_2$O$_5$ – (7.5 –x) ZnO -xFe glasses for 1.5% of Fe

The Vickers indentation image of 15Li$_2$O – 15Na$_2$O – 37.5 B$_2$O$_3$ – 25 P$_2$O$_5$ – (7.5 – x) ZnO –xFe glasses for 2.0% of Fe content is shown in fig. 4.3.12.

Fig. 4.3.12. Vickers indentation image of 15Li$_2$O – 15Na$_2$O – 37.5 B$_2$O$_3$ – 25 P$_2$O$_5$ – (7.5 –x) ZnO -xFe glasses for 2.0% of Fe

4.3.2.7 Refractive Index

The refractive indices of the prepared 15Li$_2$O – 15Na$_2$O – 37.5 B$_2$O$_3$ – 25 P$_2$O$_5$ – (7.5 –x) ZnO -xFe glasses were measured by travelling microscope. The measured refractive index has been 1.5382 for 0.5% Fe and 1.4210 for 1.0% Fe content doped the glasses and it agreed well with the reported value of El-Alaily et. al.
is 1.5731\textsuperscript{[40]}. However, the refractive index of our investigated samples are in the range of 1.4210 – 1.5382. These values are good agreement to the reported by Alaily et. al.

4.3.2.8 Dielectric Properties and Conductivity

The dielectric properties and a.c. conductivity measured to all glasses with varying frequency at room temperature using impedance analyser LCR-Q meter (Model HIOKI3532-50 LCR Hi- Tester) in the frequency range 100 Hz to 5MHz with accuracy 0.001Hz. The impedance analyser was interfaced to a personal computer using GPIB add on card and the recorded data was stored on the computer.

Measurements of capacitor and dissipation factor $\tan\delta$ with varying frequency. Using this value we have calculated dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$) and dielectric loss tangent ($\tan\delta$) using following relation \textsuperscript{[41]}.

$$\varepsilon' = \frac{C \rho d}{\varepsilon_0 A} \quad (1)$$

$$\varepsilon'' = \varepsilon' \tan\delta \quad (2)$$

![Dielectric constant with log frequency](image)

*Fig.4.3.13. Dielectric constant with log frequency*
Where \( d \) is thickness of glass, \( A \) area of glass and \( \varepsilon_0 \) permivitiy of free space,

The dielectric properties of glasses arise due to ionic motion. Fig 4.3.13 shows the frequency dependence of dielectric constant with room temperature of the studied samples. From fig 4.3.13 all samples show the same behaviour is observed. Dielectric constant decreases with increase in frequency up to a certain frequency and beyond this frequency that remains fairly constant the similar behaviour is reported by investigations \(^{42}\). At certain frequency dielectric constant increases with increases in Fe ion. This behaviour indicates that ferroelectric behaviour of all samples. This variation of dielectric constant attributed to polarized space charge. Since grains or grain boundaries are absent in glasses, the dielectric constants of glasses are usually low, generally 5-12 dielectric properties are governed by conductions mechanism in glasses at low frequency the dielectric constant is high this behaviour can explained on the basis of polarization process.

![Fig.4.3.14.Dielectric loss with log frequency](image-url)
Fig. 4.3.14 shows that dielectric loss in each glass is the same behaviour. Fig 4.3.15 shows the dielectric loss tangent with frequency of all samples. Fig 4.3.15 dielectric loss tangent increases with increase in frequency. The similar behaviour is obtained all glass samples.

The a.c. conductivity obtained from the following equation.

\[
\sigma_{a.c} = \omega \varepsilon \varepsilon' \tan \delta 
\]  

(3)

When a low frequency ac fields applied across a material, the free charges in the material can follow the field, giving rise to energy losses.
Fig. 4.3.16. A.C. conductivity with log frequency

Thus ac conductivity can be considered as losses due to bound charges whereas there should be no such losses under a dc field. In the present study, the ac electrical conductivity (\(\sigma_{\text{a.c.}}\)) showed frequency dependence, (\(\sigma_{\text{a.c.}}\)) Increase with frequency as shown in Fig 4.3.16. Even though, the origin of the frequency dependence on conductivity is controversial. The a.c. conductivity increase with increase in frequency and Fe ion similar type of behaviour is reported in a V\(_2\)O\(_5\) doped glass\(^{[43]}\).

4.3.2.9 Chemical Degradation

The result of the corrosion test for the polished samples of mixed alkali borophosphate glasses doped with Fe system was carried out in 10% NaOH and 10% HCl solutions at room temperature for 1hrs to 6 hrs of exposure are shown in tables 4.3.5 and 4.3.6.

The dissolution rate was seen to be higher in acidic medium as compared to alkaline medium.

In 10% HCl solution, the rate of dissolution for glass V-4 i.e. 15Li\(_2\)O – 15Na\(_2\)O – 37.5 B\(_2\)O\(_3\) – 25P\(_2\)O\(_5\) – (7.5 – x) ZnO – 2.0Fe is maximum and for glass V-1
i.e. $15\text{Li}_2\text{O} - 15\text{Na}_2\text{O} - 37.5 \ \text{B}_2\text{O}_3 - 25\text{P}_2\text{O}_5 - (7.5 - x) \ \text{ZnO} - 0.5\text{Fe}$ is less in all the studied glass samples of mixed alkali borophosphate glasses doped with Fe glasses.

In 10% NaOH solution, the dissolution rate is very slow, for V-1 glass than the other. From the studies of chemical degradation it came to notice that the rate of dissolution of V-1 glass in both i.e. in 10% HCl and in 10% NaOH is low in comparison to other investigated mixed alkali borophosphate glasses doped with Fe system.

In 10% HCl solution, the rate of dissolution for glass V-4 i.e. $15\text{Li}_2\text{O} - 15\text{Na}_2\text{O} - 37.5 \ \text{B}_2\text{O}_3 - 25\text{P}_2\text{O}_5 - (7.5 - x) \ \text{ZnO} - 2.0\text{Fe}$ is maximum and for glass V-1 i.e. $15\text{Li}_2\text{O} - 15\text{Na}_2\text{O} - 37.5 \ \text{B}_2\text{O}_3 - 25\text{P}_2\text{O}_5 - (7.5 - x) \ \text{ZnO} - 0.5\text{Fe}$ is less in all the studied glass samples of mixed alkali borophosphate glasses doped with Fe glasses.

The investigated glasses contain group I (Periodic Table) fluxes i.e. Na and glass former B$_2$O$_3$, which help to improve the chemical resistance hence the rate of dissolution in NaOH solution is slower than in HCl. The result of the corrosion test for the polished samples of mixed alkali borophosphate glasses doped with Fe system was carried out in 10% NaOH and 10% HCl solutions at room temperature for 1hrs to 6 hrs of exposure are shown in figures 4.3.17 and 4.3.18.

Table 4.3.5. Weight loss observed in 10% HCl for 1 to 6 hrs of exposure of $15\text{Li}_2\text{O} - 15\text{Na}_2\text{O} - 37.5 \ \text{B}_2\text{O}_3 - 25\text{P}_2\text{O}_5 - (7.5 - x) \ \text{ZnO} - x\text{Fe}$ glasses.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Glass Code</th>
<th>Composition X mole% of Fe</th>
<th>Wt. loss in 10% HCl g/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1 hrs</td>
</tr>
<tr>
<td>1</td>
<td>V-1</td>
<td>0.5</td>
<td>0.42</td>
</tr>
<tr>
<td>2</td>
<td>V-2</td>
<td>1.0</td>
<td>0.38</td>
</tr>
<tr>
<td>3</td>
<td>V-3</td>
<td>1.5</td>
<td>0.31</td>
</tr>
<tr>
<td>4</td>
<td>V-4</td>
<td>2.0</td>
<td>0.35</td>
</tr>
</tbody>
</table>
Table 4.3.6. Weight loss observed in 10% NaOH for 1 to 6 hrs of exposure of $15\text{Li}_2\text{O} - 15\text{Na}_2\text{O} - 37.5 \text{B}_2\text{O}_3 - 25\text{P}_2\text{O}_5 - (7.5 - x) \text{ZnO} - x\text{Fe}$ glasses.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Glass Code</th>
<th>Composition</th>
<th>X mole% of Fe</th>
<th>Wt. loss in 10% NaOH g/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1 hrs</td>
</tr>
<tr>
<td>1</td>
<td>V-1</td>
<td></td>
<td>0.5</td>
<td>0.011</td>
</tr>
<tr>
<td>2</td>
<td>V-2</td>
<td></td>
<td>1.0</td>
<td>0.015</td>
</tr>
<tr>
<td>3</td>
<td>V-3</td>
<td></td>
<td>1.5</td>
<td>0.013</td>
</tr>
<tr>
<td>4</td>
<td>V-4</td>
<td></td>
<td>2.0</td>
<td>0.012</td>
</tr>
</tbody>
</table>

Fig. 4.3.17. Plot of weight loss versus Fe content at various time of exposure in 10% HCL.
Fig. 4.3.18. Plot of weight loss versus Fe content at various time of exposure in 10% NaOH.
4.4 Studies of Mixed Alkali Borophosphate Glasses Doped with Cu

\[15\text{Li}_2\text{O} – 15\text{Na}_2\text{O} – 37.5 \text{B}_2\text{O}_3 – 25 \text{P}_2\text{O}_5 – (7.5 –x) \text{ZnO} -x\text{Cu}\]

The structures and properties of glasses in the mixed alkali (MA) borate glass doped with Cu system i.e. \(15\text{Li}_2\text{O} – 15\text{Na}_2\text{O} – 37.5 \text{B}_2\text{O}_3 – 25 \text{P}_2\text{O}_5 – (7.5 –x) \text{ZnO} -x\text{Cu}\) have been investigated.

![Photographs of investigated mixed alkali borophosphate glasses doped with Cu.](image)

4.4.1 Characterization

\[15\text{Li}_2\text{O} – 15\text{Na}_2\text{O} – 37.5 \text{B}_2\text{O}_3 – 25 \text{P}_2\text{O}_5 – (7.5 –x) \text{ZnO} -x\text{Cu}\]

The detailed characterization procedure of glass samples studies are given in chapter 2.

4.4.2 Results and Discussion

4.4.2.1. Density Measurements

It is an important tool to explore the structural compactness, softening, the change in geometric configuration and co-ordination etc. The density and molar volumes of mixed alkali borophosphate glasses doped with Cu ions under the investigations have been given in table 4.4.1. In the present glass, \(\text{Na}_2\text{O} – \text{ZnO} – \text{B}_2\text{O}_3\) content remain constant while the CuO content varies from 5 to 15 % by replacing \(\text{P}_2\text{O}_5\) content.
### Table 4.4.1. Chemical composition (mol %), density values and molar volume of mixed alkali borophosphate glasses doped with Cu ions. (15Li$_2$O – 15Na$_2$O – 37.5 B$_2$O$_3$ – 25 P$_2$O$_5$ – (7.5 –x) ZnO –xCu)

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Glass Code</th>
<th>Glass composition (Mol %)</th>
<th>Molar Mass (gm)</th>
<th>Density (g/cm$^3$)</th>
<th>Molar Volume (cc/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Li$_2$O</td>
<td>Na$_2$O</td>
<td>B$_2$O$_3$</td>
<td>P$_2$O$_5$</td>
<td>ZnO</td>
</tr>
<tr>
<td>1</td>
<td>VI-1</td>
<td>15</td>
<td>15</td>
<td>37.5</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>VI-2</td>
<td>15</td>
<td>15</td>
<td>37.5</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>VI-3</td>
<td>15</td>
<td>15</td>
<td>37.5</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>VI-4</td>
<td>15</td>
<td>15</td>
<td>37.5</td>
<td>25</td>
</tr>
<tr>
<td>5</td>
<td>VI-5</td>
<td>15</td>
<td>15</td>
<td>37.5</td>
<td>25</td>
</tr>
</tbody>
</table>

From the graph it is shown that with addition of Cu there is initial increase in density is observed. This is may be due to compactness of glass network formation.

The molar mass of the samples decreases with increasing Cu composition, the density of glass increases from 1.68 to 2.49 g/cm$^3$ and molar volume decreases from 48.42 to 32.53 cc/mol as shown in fig 4.4.1.
Fig. 4.4.1. Variation of density and molar volume with mol% of Cu ion

4.4.2.2. XRD Analysis

Powder XRD patterns of all the 15Li$_2$O – 15Na$_2$O – 37.5 B$_2$O$_3$ – 25 P$_2$O$_5$ – (7.5 – x) ZnO -xCu glass samples showed broad peaks characteristics of glass structure, amorphous nature of glass. A representative XRD pattern is shown in fig 4.4.2.
Fig 4.4.2. XRD pattern of a mixed alkali borophosphate glasses doped with Cu

\[(15\text{Li}_2\text{O} - 15\text{Na}_2\text{O} - 37.5 \text{B}_2\text{O}_3 - 25 \text{P}_2\text{O}_5 - (7.5 - x) \text{ZnO} - x\text{Cu})\]

The broad peak obtained at 2θ range of 20⁰ – 30⁰ implies the non-crystalline nature of the glass.

4.4.2.3. Infrared Transmission

Fig 4.4.3. IR spectra of the mixed alkali borophosphate glasses doped with x=1.0% Cu.
Table 4.4.2: IR peaks and their assignments for mixed alkali borophosphate glasses doped with Cu.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Wave No.</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>962 cm$^{-1}$</td>
<td>Characteristic of the vibrations of bridging P-O-P groups</td>
</tr>
<tr>
<td>2</td>
<td>1680 cm$^{-1}$</td>
<td>Assigned to water, OH</td>
</tr>
<tr>
<td>3</td>
<td>620 cm$^{-1}$</td>
<td>P-O-Cu stretching vibrations being modified into the P-O-Cu-O-Zn bands.</td>
</tr>
</tbody>
</table>

IR transmission spectra are shown in fig. 4.4.3, which represent the characteristics of the various phosphate glass samples i.e. VI-2 of % CuO doped glass. The absorption bands appear in the range 700 – 1500 cm$^{-1}$ are mainly due to the phosphate network. The pyrophosphate groups are predominant structure units in all these glasses. The identical IR spectra for all these glasses clearly indicate that the structure of PO$_4$ chains doesn’t get affected by Cu$^{+1}$ and Cu$^{+2}$ ions in the glass. These strong bands of the phosphate glass samples i.e. VI-2 of % CuO doped glass is similar to the reported work [45-47].

4.4.2.4. UV-Visible Spectroscopy

The fundamental optical band gap of the glasses has been calculated using UV-Vis transmittance spectra to understand their optically induced transition. The UV-VIS transmittance spectra of a mixed alkali borophosphate glasses doped with Cu are shown in figure 4.4.4.

The wavelength of mixed alkali borophosphate glasses doped with Cu glasses samples increases with increasing the % of Cu. It was also confirmed that energy band gap decreases with % of Cu increases. Figure 4.4.4 reveals the variation of transmittance spectra of mixed alkali borophosphate glasses doped with Cu samples.
Table 4.4.3. Band gap of different mixed alkali borophosphate glasses doped with Cu ion.

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Glass Code</th>
<th>%T</th>
<th>UV cut off (nm)</th>
<th>Band Gap in eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>VI-1</td>
<td>25346.80</td>
<td>520.08</td>
<td>2.39</td>
</tr>
<tr>
<td>2</td>
<td>VI-2</td>
<td>17121.79</td>
<td>529.41</td>
<td>2.35</td>
</tr>
<tr>
<td>3</td>
<td>VI-3</td>
<td>15548.88</td>
<td>554.95</td>
<td>2.24</td>
</tr>
</tbody>
</table>

Fig 4.4.4. UV transmission spectra of xLi$_2$O – (30-x) Na$_2$O – 37.5 B$_2$O$_3$ – 25 P$_2$O$_5$ – (7.5 –x) ZnO -xCu glasses

4.4.2.5. TGA – DTA Analysis

The characteristic temperatures of the obtained glass were determined by TGA-DTA curves that were obtained for the as quenched glasses (powder) corresponding to the compositions x=0.5%, 1.0% and 1.5% of Cu content are shown in figs. 4.4.5, 4.4.6 and 4.4.7, respectively.
Fig. 4.4.5. TGA-DTA curve and characteristic temperature determined for the compositions $x=0.5\%$ Cu glass at heating rate of 40°C/min.

Fig. 4.4.6. TGA-DTA curve and characteristic temperature determined for the compositions of $x=1.0\%$ Cu glass at heating rate of 40°C/min.
Fig. 4.4.7. TGA-DTA curve and characteristic temperature determined for the compositions of $x=1.5\%$ Cu glass at heating rate of $40^\circ C$/min.

The glass transition temperatures ($T_g$) and crystallization temperature ($T_c$) of the various $15\text{Li}_2\text{O} – 15\text{Na}_2\text{O} – 37.5 \text{B}_2\text{O}_3 – 25 \text{P}_2\text{O}_5 – (7.5 – x) \text{ZnO} – x\text{Cu}$ glass samples are listed in table 4.4.4. Metwalli et. al. [48] found that the glass transition temperature ($T_g$) is $344^\circ C$ for $50\text{B}_2\text{O}_3 – 45 \text{PbO} – 5\text{CuO}$ glass samples.

**Table 4.4.4. Transition temperatures of mixed alkali borophosphate glasses doped with Cu system indicated by TGA - DTA curves.**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Glass code</th>
<th>Mole % Cu</th>
<th>$T_g (^\circ C)$</th>
<th>$T_c (^\circ C)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>VI-1</td>
<td>0.5</td>
<td>441.92</td>
<td>502.33</td>
</tr>
<tr>
<td>2</td>
<td>VI-2</td>
<td>1.0</td>
<td>447.83</td>
<td>514.94</td>
</tr>
<tr>
<td>3</td>
<td>VI-3</td>
<td>1.5</td>
<td>444.20</td>
<td>515.08</td>
</tr>
</tbody>
</table>

From table 4.4.4 it indicates that the glass transition temperature changes with increasing the Cu content. It may be due to the change in network structure; the
material become soft of the mixed alkali borophosphate glasses doped with Cu samples.

4.4.2.6. Microhardness

The microhardness of $15\text{Li}_2\text{O} - 15\text{Na}_2\text{O} - 37.5 \text{B}_2\text{O}_3 - 25 \text{P}_2\text{O}_5 - (7.5 - x)$ ZnO -xCu glasses is 2.4517 GPa for 0.5% and 3.6285 GPa for 1.0% and 2.7459 GPa for 1.5% of Cu content. It indicates the formation of more rigid structure. Miura et. al. [49] found that the microhardness are in the range of 4.3 to 2.7 GPa for $y\text{CuO} \times(100-y)$ P$_2$O$_5$ of glass samples. The values are good agreement with the reported values.

The Vickers indentation image of $15\text{Li}_2\text{O} - 15\text{Na}_2\text{O} - 37.5 \text{B}_2\text{O}_3 - 25 \text{P}_2\text{O}_5 - (7.5 - x)$ ZnO -xCu glasses for 0.5% of Cu content is shown in fig. 4.4.8.

![Vickers indentation image of 15Li2O - 15Na2O - 37.5 B2O3 - 25 P2O5 - (7.5 -x) ZnO -xCu glasses for 0.5% of Cu content](image)

Fig.4.4.8. Vickers indentation image of $15\text{Li}_2\text{O} - 15\text{Na}_2\text{O} - 37.5 \text{B}_2\text{O}_3 - 25 \text{P}_2\text{O}_5 - (7.5 - x)$ ZnO -xCu glasses for 0.5% of Cu content

The Vickers indentation image of $15\text{Li}_2\text{O} - 15\text{Na}_2\text{O} - 37.5 \text{B}_2\text{O}_3 - 25 \text{P}_2\text{O}_5 - (7.5 - x)$ ZnO -xCu glasses for 0.5% of Fe content is shown in fig. 4.4.9.
Fig. 4.4.9. Vickers indentation image of 15Li₂O – 15Na₂O – 37.5 B₂O₃ – 25 P₂O₅ – (7.5 –x) ZnO –xCu glasses for 1.0% of Cu content

The Vickers indentation image of 15Li₂O – 15Na₂O – 37.5 B₂O₃ – 25 P₂O₅ – (7.5 –x) ZnO –xCu glasses for 0.5% of Fe content is shown in fig. 4.4.10.

Fig. 4.4.10. Vickers indentation image of 15Li₂O – 15Na₂O – 37.5 B₂O₃ – 25 P₂O₅ – (7.5 –x) ZnO –xCu glasses for 1.5% of Cu content

4.4.2.7. Refractive Index

The refractive indices of the prepared 15Li₂O – 15Na₂O – 37.5 B₂O₃ – 25 P₂O₅ – (7.5 –x) ZnO –xCu glasses were calculated a simple technique by travelling microscope. The refractive index 1.237 for 0.5% Cu, 1.262 for 1.0% Cu and 1.283 for 1.5% Cu doped glasses.
4.4.2.8. Chemical Degradation

In the determination of degradation mechanisms, it is important to outline the types of reaction that may take place between acid/alkali and phosphate glasses.

Polished samples of mixed alkali borophosphate glasses doped with Cu glasses were exposed for 1 to 6 hrs of exposure.

The plot of weight loss observed and a content of CuO listed in table 4.4.5 and 4.4.6. The dissolution rate for Cu ion doped mixed alkali borophosphate glasses was seen to be low as compared with previous glasses. It results that introduction of Cu and Zn ions increase the chemical durability.

From the observed result, it is noticed that weight loss in HCl is more than NaOH. The weight loss of investigated glass samples in NaOH is increase with increases in CuO content up to 15%; but in HCl initially the weight loss is rapidly upto 15%. Plot of weight loss versus Cu content at various time of exposure in 10% HCL are shown in figure 4.4.11. Plot of weight loss versus Cu content at various time of exposure in 10% NaOH is shown in figure 4.4.12.

Table. 4.4.5. Weight loss observed in 10% HCl for 1 to 6 hrs of exposure of 15Li$_2$O – 15Na$_2$O – 37.5 B$_2$O$_3$ – 25P$_2$O$_5$ – (7.5 – x) ZnO – xCu glasses

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Glass Code</th>
<th>X mole% of Cu</th>
<th>Wt. loss in 10% HCl g/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1 hrs</td>
</tr>
<tr>
<td>1</td>
<td>VI-1</td>
<td>0.5</td>
<td>0.50</td>
</tr>
<tr>
<td>2</td>
<td>VI-2</td>
<td>1.0</td>
<td>0.47</td>
</tr>
<tr>
<td>3</td>
<td>VI-3</td>
<td>1.5</td>
<td>0.39</td>
</tr>
</tbody>
</table>
Table 4.4.6. Weight loss observed in 10% NaOH for 1 to 6 hrs of exposure of
$15\text{Li}_2\text{O} - 15\text{Na}_2\text{O} - 37.5\text{B}_2\text{O}_3 - 25\text{P}_2\text{O}_5 - (7.5 - x)\text{ZnO} - x\text{Cu}$ glasses

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Glass Code</th>
<th>Composition X mole% of Cu</th>
<th>Wt. loss in 10% NaOH g/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1 hrs</td>
</tr>
<tr>
<td>1</td>
<td>VI-1</td>
<td>0.5</td>
<td>0.015</td>
</tr>
<tr>
<td>2</td>
<td>VI-2</td>
<td>1.0</td>
<td>0.021</td>
</tr>
<tr>
<td>3</td>
<td>VI-3</td>
<td>1.5</td>
<td>0.030</td>
</tr>
</tbody>
</table>

*Fig. 4.4.11. Plot of weight loss versus Cu content at various time of exposure in 10% HCL.*
Fig. 4.4.12. Plot of weight loss versus Cu content at various time of exposure in 10% NaOH.
4.5 Studies of Mixed Alkali (MA) Borophosphate Glasses Doped with TiO$_2$

$15\text{Li}_2\text{O} – 15\text{Na}_2\text{O} – 37.5\text{B}_2\text{O}_3 – 25\text{P}_2\text{O}_5 – (7.5 – x)\text{ZnO} – x\text{TiO}_2$

The structures and properties of glasses in the mixed alkali borophosphate glasses doped with TiO$_2$ system i.e. $15\text{Li}_2\text{O} – 15\text{Na}_2\text{O} – 37.5\text{B}_2\text{O}_3 – 25\text{P}_2\text{O}_5 – (7.5 – x)\text{ZnO} – x\text{TiO}_2$ have been investigated.

Photographs of investigated mixed alkali borophosphate glasses doped with TiO$_2$

4.5.1 Characterization

$15\text{Li}_2\text{O} – 15\text{Na}_2\text{O} – 37.5\text{B}_2\text{O}_3 – 25\text{P}_2\text{O}_5 – (7.5 – x)\text{ZnO} – x\text{TiO}_2$

The detailed characterization procedure is given in chapter 2.

4.5.2 Results and Discussion

4.5.2.1 Density Measurements

The mixed alkali borophosphate glasses doped with TiO$_2$ ions under the investigations have been displayed in table 4.5.1.
Table 4.5.1- density and molar volume of $15\text{Li}_2\text{O} - 15\text{Na}_2\text{O} - 37.5\text{B}_2\text{O}_3 - 25\text{P}_2\text{O}_5 - (7.5 - x)\text{ZnO} - x\text{TiO}_2$ glass system

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Glass Code</th>
<th>Glass composition (Mol %)</th>
<th>Molar Mass (gm)</th>
<th>Density (g/cm$^3$)</th>
<th>Molar Volume (cc/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Li$_2$O</td>
<td>Na$_2$O</td>
<td>B$_2$O$_3$</td>
<td>P$_2$O$_5$</td>
</tr>
<tr>
<td>1</td>
<td>VII-1</td>
<td>15</td>
<td>15</td>
<td>37.5</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>VII-2</td>
<td>15</td>
<td>15</td>
<td>37.5</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>VII-3</td>
<td>15</td>
<td>15</td>
<td>37.5</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>VII-4</td>
<td>15</td>
<td>15</td>
<td>37.5</td>
<td>25</td>
</tr>
<tr>
<td>5</td>
<td>VII-5</td>
<td>15</td>
<td>15</td>
<td>37.5</td>
<td>25</td>
</tr>
</tbody>
</table>

From the table for glass samples indicates the density of glass increases from 1.65 to 1.82 g/cm$^3$ and molar volume decreases from 49.35 to 44.73 cc/mol as noted in a table and plotted density vs. content of TiO$_2$ is as shown in fig 4.5.1. Increased in modifier contents introduce the formation of NBO containing borate triangles $^{[50-52]}$. With addition of TiO$_2$ the topology of the network is changes. The increase of the modifier contents i.e. TiO$_2$ acts as glass modifier. These results are found in good agreement with results reported earlier $^{[53-55]}$. 
Fig. 4.5.1. Variation of density and molar volume with mol % of TiO$_2$ ion

4.5.2.2. XRD Analysis

The XRD patterns of all the mixed alkali borophosphate glasses doped with TiO$_2$ samples show no sharp peak, but only a broad diffuse hump around low angle region, this is clear indication of glass structure. Representative XRD pattern is shown in fig 4.5.2, which confirms the amorphous nature of the investigated glass samples.
Fig. 4.5.2. XRD pattern of a mixed alkali borophosphate glasses doped with TiO$_2$

$(15\text{Li}_2\text{O} – 15\text{Na}_2\text{O} – 37.5 \text{B}_2\text{O}_3 – 25 \text{P}_2\text{O}_5 – (7.5 – x) \text{ZnO} – x\text{TiO}_2)$ samples

4.5.2.3. Infrared Transmission

Fig. 4.5.3. IR Spectra of mixed alkali borophosphate glasses doped with $x=1.5\%$ TiO$_2$
Table 4.5.2 IR peaks and their assignments for mixed alkali borophosphate glasses doped with TiO₂

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Wave No.</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1713 cm⁻¹</td>
<td>Asymmetric stretching vibration of PO₂ groups</td>
</tr>
<tr>
<td>2</td>
<td>1548 and 1417 cm⁻¹</td>
<td>Asymmetric and symmetric stretching of PO₃ groups</td>
</tr>
<tr>
<td>3</td>
<td>1016 cm⁻¹</td>
<td>Asymmetric stretching of P-O-P bridges</td>
</tr>
<tr>
<td>4</td>
<td>591 and 571 cm⁻¹</td>
<td>Symmetric stretching of P-O-P bridges</td>
</tr>
<tr>
<td>5</td>
<td>518 cm⁻¹</td>
<td>P-O bonds</td>
</tr>
</tbody>
</table>

Symmetric stretching mode of PO₃ units is due to weak band at 1016 cm⁻¹; these bands are characteristic absorptions of BO₄ structural units and band observed at 1417 cm⁻¹ is a characteristic absorption of BO₃ structural units [56-58].

4.5.2.4. UV-Visible Spectroscopy

The glasses with and without TiO₂ doping have been characterized with UV–visible spectrophotometer and it has shown interesting results. Fig. 4.5.4 represents the transmittance spectra of the x=1.0% and x=1.5% TiO₂ doped polished glass samples.
**Fig. 4.5.4.** UV spectra of mixed alkali borophosphate glasses doped with TiO$_2$ (15Li$_2$O – 15Na$_2$O – 37.5 B$_2$O$_3$ – 25 P$_2$O$_5$ – (7.5 – x) ZnO – x TiO$_2$) glass samples.

**Table 4.5.3.** Band gap of different mixed alkali borophosphate glasses doped with TiO$_2$

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Sample Code</th>
<th>Composition X mole %</th>
<th>% T</th>
<th>UV cut off (nm)</th>
<th>Band Gap in eV.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>VII-1</td>
<td>1.0</td>
<td>14.56</td>
<td>414.92</td>
<td>2.99</td>
</tr>
<tr>
<td>2</td>
<td>VII-2</td>
<td>1.5</td>
<td>172.53</td>
<td>434.82</td>
<td>2.86</td>
</tr>
</tbody>
</table>

The UV-VIS transmittance spectra of a mixed alkali borophosphate glasses doped with TiO$_2$ are shown in figure 4.5.4.

The wavelength of mixed alkali borophosphate glasses doped with TiO$_2$ glasses samples increases with increasing the % of TiO$_2$. It was also confirmed that energy band gap decreases with % of TiO$_2$ increases. Figure 4.5.4 reveals the variation of transmittance spectra of mixed alkali borophosphate glasses doped with TiO$_2$.
samples. This can be attributed to the structural changes that are taking place with introduction of TiO$_2$ ions.

4.5.2.5. TGA-DTA Analysis

The TGA-DTA curves that were obtained for the as quenched glasses (powder) corresponding to the compositions $x=1.0\%$ and $1.5\%$ of TiO$_2$ are shown in figs. 4.5.5 and 4.5.6, respectively.

![TGA-DTA curve and characteristic temperature determined for the compositions of $x=1.0\%$ TiO$_2$ glass at heating rate of 40°C/min.](image)

**Fig.4.5.5.** TGA-DTA curve and characteristic temperature determined for the compositions of $x=1.0\%$ TiO$_2$ glass at heating rate of 40°C/min.
The T\textsubscript{g} and T\textsubscript{c} of the various 15Li\textsubscript{2}O – 15Na\textsubscript{2}O – 37.5 B\textsubscript{2}O\textsubscript{3} – 25 P\textsubscript{2}O\textsubscript{5} – (7.5 – x) ZnO - xTiO\textsubscript{2} glass samples are listed in table 4.5.4. Shaim et. al.\textsuperscript{[59]} reported that the glass transition temperature (T\textsubscript{g}) is 440\textdegree C for Na\textsubscript{2}O – Bi\textsubscript{2}O\textsubscript{3} – P\textsubscript{2}O\textsubscript{5} – TiO\textsubscript{2} samples. This value is consistent with our values of the samples.

**Table 4.5.4. Transition temperatures of mixed alkali borophosphate glasses doped with TiO\textsubscript{2} system indicated by TGA - DTA curves.**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Glass code</th>
<th>Mole % TiO\textsubscript{2}</th>
<th>T\textsubscript{g} (\textdegree C)</th>
<th>T\textsubscript{c} (\textdegree C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>VII-1</td>
<td>1.0</td>
<td>460.73</td>
<td>525.16</td>
</tr>
<tr>
<td>2</td>
<td>VII-2</td>
<td>1.5</td>
<td>462.98</td>
<td>525.87</td>
</tr>
</tbody>
</table>

From table 4.5.4 T\textsubscript{g} increase with increasing the TiO\textsubscript{2} content. It may be due the material become soft of the sodium borate glass samples. However, the crystallization temperature (T\textsubscript{c}) increases with increasing TiO\textsubscript{2} content of the mixed alkali borophosphate glasses doped with TiO\textsubscript{2} samples it indicates larger changes in glass structure occur.
4.5.2.6. Microhardness

The microhardness of 15Li₂O – 15Na₂O – 37.5 B₂O₃ – 25 P₂O₅ – (7.5 –x) ZnO - xTiO₂ glasses is 3.1382 GPa for 1.0% and 2.9000 GPa for 1.5% of TiO₂. It indicates the formation of more rigid structure.

Vickers indentation image of 15Li₂O –15Na₂O –37.5 B₂O₃–25 P₂O₅ –(7.5 –x) ZnO-xFe glasses for 1.0% of TiO₂ content as shown in figure 4.5.7.

![Image](image1.png)

**Fig.4.5.7. Vickers indentation image of 15Li₂O – 15Na₂O – 37.5 B₂O₃ – 25 P₂O₅ – (7.5 –x) ZnO -xFe glasses for 1.0% of TiO₂ content**

Vickers indentation image of 15Li₂O –15Na₂O –37.5 B₂O₃–25 P₂O₅ –(7.5 –x) ZnO-xFe glasses for 1.5% of TiO₂ content as shown in figure 4.5.8.

![Image](image2.png)

**Fig.4.5.8. Vickers indentation image of 15Li₂O – 15Na₂O – 37.5 B₂O₃ – 25 P₂O₅ – (7.5 –x) ZnO -xFe glasses for 1.5% of TiO₂ content**
4.5.2.7. Refractive Index

The refractive indices of the prepared 15Li$_2$O – 15Na$_2$O – 37.5 B$_2$O$_3$ – 25 P$_2$O$_5$ – (7.5 – $x$) ZnO – $x$TiO$_2$ glasses were calculated by simple technique of travelling microscope. The measured refractive index has been 1.662 for 1.0% TiO$_2$ and 1.521 for 1.5% TiO$_2$ doped glasses.

4.5.2.8. Chemical Degradation

The result of the corrosion test for the polished samples of mixed alkali borophosphate glasses doped with TiO$_2$ glasses were carried out in 10% NaOH and 10% HCl solutions at room temperature for 1 hrs to 6 hrs of exposure are shown in table 4.5.5 and 4.5.6.

The dissolution rate was seen to be higher in acidic medium as compared to alkaline medium.

In 10% HCl solution, the rate of dissolution for glass VII-3 i.e. 15Li$_2$O – 15Na$_2$O – 37.5 B$_2$O$_3$ – 25P$_2$O$_5$ – (7.5 – $x$) ZnO – 2.0TiO$_2$ is maximum and for glass VII-1 i.e. 15Li$_2$O – 15Na$_2$O – 37.5 B$_2$O$_3$ – 25P$_2$O$_5$ – (7.5 – $x$) ZnO – 1.0TiO$_2$ is less in all the studied glass samples of mixed alkali borophosphate glasses doped with TiO$_2$ glasses.

In 10% NaOH solution, the dissolution rate is very slow, for VII-1 glass than the other. From the studies of chemical degradation it came to notice that the rate of dissolution of VII-1 glass in both i.e. in 10% HCl and in 10% NaOH is low in comparison to other investigated sodium borate glasses.

NaOH attack the borate skeleton; it does not attack on the alkali ions of the glasses. Due to breaking the borate skeleton more alkali released to join the attack on the glass. In 10% HCl solution, the rate of dissolution of for glass VII-3 i.e. 15Li$_2$O – 15Na$_2$O – 37.5 B$_2$O$_3$ – 25P$_2$O$_5$ – (7.5 – $x$) ZnO – 2.0TiO$_2$ is maximum and for glass VII-1 i.e. 15Li$_2$O – 15Na$_2$O – 37.5 B$_2$O$_3$ – 25P$_2$O$_5$ – (7.5 – $x$) ZnO – 1.0TiO$_2$ is less in all the studied glass samples of mixed alkali borophosphate glasses doped with TiO$_2$ glasses.

The investigated glasses contain group I (Periodic Table) fluxes i.e. Na and glass former B$_2$O$_3$, which help to improve the chemical resistance hence the rate of dissolution in NaOH solution is slower than in HCl. Plot of weight loss versus TiO$_2$ content at various time of exposure in 10% HCL is shown in figure 4.5.9. Plot of
weight loss versus TiO$_2$ content at various time of exposure in 10% HCL is shown in figure 4.5.10.

Table 4.5.5. Weight loss observed in 10% HCl for 1 to 6 hrs of exposure of 15Li$_2$O – 15Na$_2$O – 37.5 B$_2$O$_3$ – 25P$_2$O$_5$ – (7.5 – x) ZnO – xTiO$_2$ glasses

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Glass Code</th>
<th>Composition X mole% of TiO$_2$</th>
<th>Wt. loss in 10% HCl g/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1 hrs</td>
</tr>
<tr>
<td>1</td>
<td>VII-1</td>
<td>1.0</td>
<td>0.40</td>
</tr>
<tr>
<td>2</td>
<td>VII-2</td>
<td>1.5</td>
<td>0.48</td>
</tr>
<tr>
<td>3</td>
<td>VII-3</td>
<td>2.0</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Table 4.5.6. Weight loss observed in 10% NaOH for 1 to 6 hrs of exposure of 15Li$_2$O – 15Na$_2$O – 37.5 B$_2$O$_3$ – 25P$_2$O$_5$ – (7.5 – x) ZnO – xTiO$_2$ glasses

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Glass Code</th>
<th>Composition X mole% of TiO$_2$</th>
<th>Wt. loss in 10% NaOH g/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1 hrs</td>
</tr>
<tr>
<td>1</td>
<td>VII-1</td>
<td>1.0</td>
<td>0.06</td>
</tr>
<tr>
<td>2</td>
<td>VII-2</td>
<td>1.5</td>
<td>0.011</td>
</tr>
<tr>
<td>3</td>
<td>VII-3</td>
<td>2.0</td>
<td>0.014</td>
</tr>
</tbody>
</table>
Fig. 4.5.9. Plot of weight loss versus TiO$_2$ content at various time of exposure in 10% HCl.

Fig. 4.5.10. Plot of weight loss versus TiO$_2$ content at various time of exposure in 10% HCl.
References:


