2.1 Introduction

In this chapter, the experimental techniques used for both synthesis and characterization for different investigations are discussed together with relevant theory and working principle. The experimental set up used for glass preparation was grinder mixer, muffle furnace for quenching, annealing furnace etc. For structure studies techniques employed were density, molar volume, X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy. Thermal gravimetric analysis- Differential thermal analysis (TGA-DTA), microhardness test, refractive index, chemical degradation, dielectric properties and A.C. conductivity, optical investigations were carried out by UV-Spectrophotometer.

The experimental results presented in next chapter are based on the experimental procedures outlined in this chapter.

2.2 Glass Preparation

Different techniques have been used to prepare glass materials in various forms like bulk, sheet, powder, thin films, etc [1]. Melt quench technique is the simple and widely used for the preparation of glassy materials.

In principle any substance can be made into a glass provided it is cooled from its liquid state fast enough to prevent crystallization. In actual practice, glass formation has been achieved with relatively limited number of substances.

By using conventional melt-quench technique glasses were prepared. 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 aget 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.

A binary, ternary and multi-component glass systems were prepared using analytical grade compounds like NaNO₃, (NH₄)₂ HPO₄, H₃BO₃, Li₂CO₃, ZnO, Fe, Cu,
TiO$_2$ etc. The purity, make and the role of the particular component is mentioned in the table 2.2.1.

*Table 2.2.1 Raw materials used for experimental procedure.*

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>Name of the chemical</th>
<th>Make</th>
<th>% Purity</th>
<th>Role in the glass system</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H$_3$BO$_3$</td>
<td>SD Fine</td>
<td>99.5</td>
<td>Network modifier &amp; Glass former</td>
</tr>
<tr>
<td>2</td>
<td>(NH$_4$)$_2$ HPO$_4$</td>
<td>SD Fine</td>
<td>98</td>
<td>Glass former</td>
</tr>
<tr>
<td>3</td>
<td>NaNO$_3$</td>
<td>SD Fine</td>
<td>99.5</td>
<td>Network modifier</td>
</tr>
<tr>
<td>4</td>
<td>Li$_2$CO$_3$</td>
<td>SD Fine</td>
<td>99</td>
<td>Network modifier</td>
</tr>
<tr>
<td>5</td>
<td>ZnO</td>
<td>SD Fine</td>
<td>99</td>
<td>Network modifier</td>
</tr>
<tr>
<td>6</td>
<td>Fe</td>
<td>Merck</td>
<td>98</td>
<td>Colorant</td>
</tr>
<tr>
<td>7</td>
<td>Cu</td>
<td>RL Fine</td>
<td>99</td>
<td>Colorant</td>
</tr>
<tr>
<td>8</td>
<td>TiO$_2$</td>
<td>Qualigens Fine</td>
<td>98</td>
<td>Colorant</td>
</tr>
</tbody>
</table>

### 2.2.1 Batch Preparations

The glass composition was weighed according to weight percent to give a 30gm batch as given in table 2.2.2. (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.
Table 2.2.2 Weight of compound required for 1 gm of their oxides.

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Compound</th>
<th>Molecular weight</th>
<th>Dissociation temp. M.P. °C</th>
<th>Corresponding Oxide</th>
<th>Mole. Wt. of oxide</th>
<th>Wt. of compound for 1 gm of oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H₃BO₃</td>
<td>61.81</td>
<td>160°C</td>
<td>B₂O₃</td>
<td>69.68</td>
<td>1.774</td>
</tr>
<tr>
<td>2</td>
<td>NaNO₃</td>
<td>84.99</td>
<td>306°C</td>
<td>Na₂O</td>
<td>62.0</td>
<td>2.741</td>
</tr>
<tr>
<td>3</td>
<td>(NH₄)₂HPO₄</td>
<td>263.94</td>
<td>198°C</td>
<td>P₂O₅</td>
<td>141.94</td>
<td>1.859</td>
</tr>
<tr>
<td>4</td>
<td>Li₂CO₃</td>
<td>73.89</td>
<td>618°C</td>
<td>Li₂O</td>
<td>29.88</td>
<td>2.473</td>
</tr>
<tr>
<td>5</td>
<td>ZnO</td>
<td>81.38</td>
<td>390°C</td>
<td>ZnO</td>
<td>81.38</td>
<td>1.00</td>
</tr>
<tr>
<td>6</td>
<td>Fe</td>
<td>55.85</td>
<td>1535°C</td>
<td>Fe</td>
<td>55.85</td>
<td>1.00</td>
</tr>
<tr>
<td>7</td>
<td>Cu</td>
<td>63.55</td>
<td>1083°C</td>
<td>Cu</td>
<td>63.55</td>
<td>1.00</td>
</tr>
<tr>
<td>8</td>
<td>TiO₂</td>
<td>80.00</td>
<td>1675°C</td>
<td>TiO₂</td>
<td>80.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

For example, let us consider diammonium hydrogen phosphate and sodium nitrate, which incorporates in glass network as P₂O₅ and Na₂O respectively.

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

\[
2(NH₄)₂HPO₄ \rightarrow P₂O₅ + 2H₂O + 4NH₃ \uparrow + \frac{1}{2} O₂ \uparrow + \frac{1}{2} H₂
\]

\[
2(NH₄)₂HPO₄ \equiv 1P₂O₅
\]

2 [molecular weight of (NH₄)₂HPO₄] \equiv 1 [molecular weight of P₂O₅]

2 [131.97 gm of DAP] \equiv 1 [141.94 gm of P₂O₅]

263.94 gm of DAP \equiv 141.94 gm of P₂O₅

1.8595 gm of DAP \equiv 1 gm of P₂O₅

Thus 1.8595 gm of (NH₄)₂HPO₄ dissociates to form 1 gm P₂O₅

a) Sodium nitrate (NaNO₃) dissociates at 306°C as follows –

\[
2NaNO₃ \rightarrow Na₂O + 2NO₂ \uparrow + \frac{1}{2} O₂ \uparrow
\]

\[
2NaNO₃ \equiv 1Na₂O
\]

2 [molecular weight of NaNO₃] \equiv 1 [molecular weight of Na₂O]

2 [84.99 gm of NaNO₃] \equiv 1 [62 gm of Na₂O]

169.98 gm of NaNO₃ \equiv 62 gm of Na₂O
2.7416 gm of NaNO₃ ≡ 1 gm of Na₂O
Thus 2.7416 gm of NaNO₃ dissociation to form 1 gm Na₂O

Similarly, the dissociation reactions of different compounds to form 1 gm of their respective oxides are tabulated in table 2.2.2.

2.2.2 Batch Calculation
An example of batch calculation may be explained here for

X Na₂O – (100 – X) B₂O₃ glass system,

Where, X = 25, 30, 35, 40, 45 mole% of Na₂O
Glass composition –

<table>
<thead>
<tr>
<th></th>
<th>Mole %</th>
<th>30</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mole. wt.</td>
<td>62</td>
<td>69.62</td>
<td></td>
</tr>
<tr>
<td>Wt / mole</td>
<td>18.6</td>
<td>48.73</td>
<td></td>
</tr>
</tbody>
</table>

Step– I – Calculation of wt / mole

For Na₂O

100% Na₂O contains 62 gm of Na₂O
Then, 30% of Na₂O contains how much gm of Na₂O
Hence, 100% of Na₂O ≡ 62 gm of Na₂O

30% of Na₂O ≡ X gm of Na₂O
X ≡ 62×30/100
X ≡ 18.6 gm of Na₂O

For B₂O₃

100% of B₂O₃ contains 69.62 gm of B₂O₃
Then, 70% of B₂O₃ contains how much gm of B₂O₃
Hence, 100% of B₂O₃ ≡ 69.62 gm of B₂O₃

70% of B₂O₃ ≡ Y gm of B₂O₃
Y ≡ 69.62 × 70/100
Y ≡ 48.73 gm of B₂O₃
Step – II – Calculation of molecular weight of sample

Molecular weight of respective glass sample is nothing but the summation of wt / mole of the constituent oxides of glass sample
i.e. molecular weight of 30 Na₂O – 70 B₂O₃ ≡ wt / mole of Na₂O + wt / mole of B₂O₃
Glass sample
≡ X + Y
≡ 18.6 + 48.73
Hence, molecular weight of 30 Na₂O – 70 B₂O₃ glass sample ≡ 67.33gm.

Step – III – Calculation of quantity of oxides for 30 gm batch

This glass composition contains 18.6 gm Na₂O and 48.73 gm of B₂O₃, total weight is 67.33gm which is its molecular weight. Now this 67.33 gm converts to 30 gm batch.
For Na₂O –
67.33 gm of sample ≡ 18.6 gm of Na₂O
30 gm of sample ≡ x’ gm of Na₂O
x’ ≡ 18.6 × 30/67.33
x’ ≡ 8.28 gm of Na₂O
For B₂O₃ –
67.33 gm of sample ≡ 48.73 gm of B₂O₃
30 gm of sample ≡ y’ gm of B₂O₃
y’ ≡ 48.73×30/67.33
y’ ≡ 21.71 gm of B₂O₃
Hence, 30 gm batch of sample contains
8.28 gm of Na₂O + 21.71 gm of B₂O₃ ≡ 30 gm

Step – IV – Calculation of weight of compounds (raw materials) required for the batch

For Na₂O
NaNO₃ is used as a raw material, which dissociates at 306°C as follows –
2 NaNO₃ → Na₂O + 2NO₂ ↑ + ½ O₂↑

\[
\begin{align*}
2 \times 85 & \quad 62 \\
62 \text{ gm of Na}_2\text{O} & \equiv 2 \times 85 \text{ gm of NaNO}_3 \\
8.28 \text{ gm of Na}_2\text{O} & \equiv x'' \text{ gm of NaNO}_3 \\
x'' & \equiv 2 \times 85 \times 8.28/62 \\
x'' & \equiv 22.70 \text{ gm of NaNO}_3
\end{align*}
\]

For B₂O₃ –

\[
\begin{align*}
2 \text{ H}_3\text{BO}_3 & \rightarrow \text{B}_2\text{O}_3 + 3\text{H}_2\text{O} ↑ \\
2 \times 61.81 & \quad 69.62 \\
69.62 \text{ gm of B}_2\text{O}_3 & \equiv 2 \times 61.81 \text{ gm of H}_3\text{BO}_3 \\
21.71 \text{ gm of B}_2\text{O}_3 & \equiv y'' \text{ gm of H}_3\text{BO}_3 \\
y'' & \equiv 2 \times 61.81 \times 21.71/69.62 \\
y'' & \equiv 38.54 \text{ gm of H}_3\text{BO}_3
\end{align*}
\]

[The required raw material can also be calculated by using the data from table 2.2 as follows]

1 gm of Na₂O required 2.741 gm of NaNO₃

\[
\begin{align*}
\text{8.28 gm of Na}_2\text{O require?} \\
1 \text{ gm Na}_2\text{O} & \equiv 2.741 \text{ gm of NaNO}_3 \\
8.28 \text{ gm Na}_2\text{O} & \equiv ?\text{gm of NaNO}_3 \\
& \equiv 8.28 \times 2.741/1 \\
& \equiv 22.69 \text{ gm of NaNO}_3
\end{align*}
\]

Similarly,

\[
\begin{align*}
1 \text{ gm B}_2\text{O}_3 & \equiv 1.774 \text{ gm of H}_3\text{BO}_3 \\
21.71 \text{ gm B}_2\text{O}_3 & \equiv ?\text{gm of H}_3\text{BO}_3 \\
& \equiv 1.774 \times 21.71/1 \\
& \equiv 38.51 \text{ gm of H}_3\text{BO}_3
\end{align*}
\]

### 2.2.3 Batch Composition

30 gm batch of 30 Na₂O – 70 B₂O₃ glass system contains quantities of the raw material as – 22.70 gm of NaNO₃ and 38.54 gm of H₃BO₃ Similarly, the quantities of the initial constituents for other systems can also determined which are given in table 2.2.3 to 2.2.9.
Borate Glasses
Details of the glass compositions tried –

Table 2.2.3. For X Na₂O – (100-X) B₂O₃ glass system.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Composition</th>
<th>Mole wt. of sample</th>
<th>Wt. of raw material required for 30 gm batch of sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X Na₂O – (100-X) B₂O₃</td>
<td></td>
<td>NaNO₃</td>
</tr>
<tr>
<td>1</td>
<td>25 Na₂O – 75 B₂O₃</td>
<td>67.71</td>
<td>18.80</td>
</tr>
<tr>
<td>2</td>
<td>30 Na₂O – 70 B₂O₃</td>
<td>67.33</td>
<td>22.70</td>
</tr>
<tr>
<td>3</td>
<td>35 Na₂O – 65 B₂O₃</td>
<td>66.95</td>
<td>26.65</td>
</tr>
<tr>
<td>4</td>
<td>40 Na₂O – 60 B₂O₃</td>
<td>66.57</td>
<td>30.62</td>
</tr>
<tr>
<td>5</td>
<td>45 Na₂O – 55 B₂O₃</td>
<td>66.19</td>
<td>31.36</td>
</tr>
</tbody>
</table>

Table 2.2.4. For 30 Na₂O – (70 – X) B₂O₃ – X P₂O₅ glass system.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Composition</th>
<th>Mole Wt. of sample</th>
<th>Wt. of raw material required for 30 gm batch of sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30 Na₂O – (70 – X) B₂O₃ – X P₂O₅</td>
<td></td>
<td>NaNO₃</td>
</tr>
<tr>
<td>1</td>
<td>30 Na₂O – 55B₂O₃ – 15P₂O₅</td>
<td>78.18</td>
<td>19.55</td>
</tr>
<tr>
<td>2</td>
<td>30 Na₂O – 50B₂O₃ – 20P₂O₅</td>
<td>81.79</td>
<td>18.7</td>
</tr>
<tr>
<td>3</td>
<td>30 Na₂O – 45B₂O₃ – 25P₂O₅</td>
<td>85.4</td>
<td>17.90</td>
</tr>
<tr>
<td>4</td>
<td>30 Na₂O – 40B₂O₃ – 30P₂O₅</td>
<td>89.02</td>
<td>17.16</td>
</tr>
<tr>
<td>5</td>
<td>30 Na₂O – 35B₂O₃ – 35P₂O₅</td>
<td>92.63</td>
<td>16.50</td>
</tr>
</tbody>
</table>
Table 2.2.5. For $30 \text{Na}_2\text{O} - (45 - X) \text{B}_2\text{O}_3 - 25 \text{P}_2\text{O}_5 - X \text{ZnO}$ glass system.

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Composition mole 30 Na$_2$O – (45 – X) B$_2$O$_3$ – 25 P$_2$O$_5$ – X ZnO</th>
<th>Mole wt. Sample</th>
<th>Wt. of raw materials required for 30 gm batch of sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>NaNO$_3$ H$_3$BO$_3$ (NH$_4$)$_2$ HPO$_4$ ZnO</td>
</tr>
<tr>
<td>1</td>
<td>30Na$_2$O–42.5B$_2$O$_3$–25P$_2$O$_5$–2.5ZnO</td>
<td>85.69</td>
<td>17.85 18.37 23.09 0.71</td>
</tr>
<tr>
<td>2</td>
<td>30Na$_2$O–40B$_2$O$_3$–25P$_2$O$_5$–5ZnO</td>
<td>85.98</td>
<td>17.76 17.24 23.00 1.41</td>
</tr>
<tr>
<td>3</td>
<td>30Na$_2$O–37.5B$_2$O$_3$–25P$_2$O$_5$–7.5ZnO</td>
<td>86.28</td>
<td>17.71 16.10 22.92 2.12</td>
</tr>
<tr>
<td>4</td>
<td>30Na$_2$O–35B$_2$O$_3$–25P$_2$O$_5$–10ZnO</td>
<td>86.57</td>
<td>17.65 14.98 22.85 2.82</td>
</tr>
<tr>
<td>5</td>
<td>30Na$_2$O–32.5B$_2$O$_3$–25P$_2$O$_5$–12.5ZnO</td>
<td>86.87</td>
<td>17.60 13.86 22.77 3.51</td>
</tr>
</tbody>
</table>
Table 2.2.6. For $X \text{Li}_2\text{O} - (30 - X) \text{Na}_2\text{O} - 37.5 \text{B}_2\text{O}_3 - 25 \text{P}_2\text{O}_5 - 7.5 \text{ZnO}$ glass system.

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Composition X Li$_2$O $-(30 - X)$ Na$_2$O $-37.5$ B$_2$O$_3$ $-25$ P$_2$O$_5$ $-7.5$ ZnO</th>
<th>Mole wt. of sample</th>
<th>Wt of raw material required for 30 gm Batch</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Li$_2$CO$_3$</td>
<td>NaNO$_3$</td>
</tr>
<tr>
<td>1</td>
<td>5Li$_2$O $-25$Na$_2$O $-37.5$B$_2$O$_3$ $-25$P$_2$O$_5$ $-7.5$ZnO</td>
<td>84.67</td>
<td>1.28</td>
</tr>
<tr>
<td>2</td>
<td>10Li$_2$O $-20$Na$_2$O $-37.5$B$_2$O$_3$ $-25$P$_2$O$_5$ $-7.5$ZnO</td>
<td>83.06</td>
<td>2.64</td>
</tr>
<tr>
<td>3</td>
<td>15Li$_2$O $-15$Na$_2$O $-37.5$B$_2$O$_3$ $-25$P$_2$O$_5$ $-7.5$ZnO</td>
<td>81.46</td>
<td>3.31</td>
</tr>
<tr>
<td>4</td>
<td>20Li$_2$O $-10$Na$_2$O $-37.5$B$_2$O$_3$ $-25$P$_2$O$_5$ $-7.5$ZnO</td>
<td>79.85</td>
<td>5.53</td>
</tr>
<tr>
<td>5</td>
<td>25Li$_2$O $-5$Na$_2$O $-37.5$B$_2$O$_3$ $-25$P$_2$O$_5$ $-7.5$ZnO</td>
<td>78.25</td>
<td>7.07</td>
</tr>
</tbody>
</table>
Table 2.2.7. For 15 Li$_2$O – 15 Na$_2$O – 37.5 B$_2$O$_3$ – 25 P$_2$O$_5$ – (7.5 – X) ZnO – x Fe glass system.

<table>
<thead>
<tr>
<th>Sr No</th>
<th>Composition</th>
<th>Mole Wt. of Sample</th>
<th>Wt of raw material required for 30 gm Batch</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15 Li$_2$O – 15 Na$_2$O – 37.5 B$_2$O$_3$ – 25 P$_2$O$_5$ – (7.5 – X) ZnO – x Fe</td>
<td>Li$_2$CO$_3$</td>
<td>NaNO$_3$</td>
</tr>
<tr>
<td>1</td>
<td>15Li$_2$O – 15Na$_2$O – 37.5B$_2$O$_3$ – 25P$_2$O$_5$ – 7.0ZnO – 0.5Fe</td>
<td>81.32</td>
<td>4.08</td>
</tr>
<tr>
<td>2</td>
<td>15Li$_2$O – 15Na$_2$O – 37.5B$_2$O$_3$ – 25P$_2$O$_5$ – 6.5ZnO – 1.0Fe</td>
<td>81.19</td>
<td>4.08</td>
</tr>
<tr>
<td>3</td>
<td>15Li$_2$O – 15Na$_2$O – 37.5B$_2$O$_3$ – 25P$_2$O$_5$ – 6.0ZnO – 1.5Fe</td>
<td>81.07</td>
<td>4.08</td>
</tr>
<tr>
<td>4</td>
<td>15Li$_2$O – 15Na$_2$O – 37.5B$_2$O$_3$ – 25P$_2$O$_5$ – 5.5ZnO – 2.0Fe</td>
<td>80.94</td>
<td>4.10</td>
</tr>
<tr>
<td>5</td>
<td>15Li$_2$O – 15Na$_2$O – 37.5B$_2$O$_3$ – 25P$_2$O$_5$ – 5.0ZnO – 2.5Fe</td>
<td>80.81</td>
<td>4.10</td>
</tr>
</tbody>
</table>
**Table 2.2.8.** For $15 \text{Li}_2\text{O} - 15 \text{Na}_2\text{O} - 37.5 \text{B}_2\text{O}_3 - 25 \text{P}_2\text{O}_5 - (7.5 - X) \text{ZnO} - x \text{Cu}$

glass system.

<table>
<thead>
<tr>
<th>Sr No</th>
<th>Composition</th>
<th>Mole Wt. of Sample</th>
<th>Wt of raw material required for 30 gm Batch</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Li$_2$CO$_3$</td>
</tr>
<tr>
<td>1</td>
<td>15Li$_2$O – 15Na$_2$O – 37.5B$_2$O$_3$ – 25P$_2$O$_5$ – 7.0ZnO – 0.5Cu</td>
<td>81.36</td>
<td>4.08</td>
</tr>
<tr>
<td>2</td>
<td>15Li$_2$O – 15Na$_2$O – 37.5B$_2$O$_3$ – 25P$_2$O$_5$ – 6.5ZnO – 1.0Cu</td>
<td>81.27</td>
<td>4.08</td>
</tr>
<tr>
<td>3</td>
<td>15Li$_2$O – 15Na$_2$O – 37.5B$_2$O$_3$ – 25P$_2$O$_5$ – 6.0ZnO – 1.5Cu</td>
<td>81.19</td>
<td>4.08</td>
</tr>
<tr>
<td>4</td>
<td>15Li$_2$O – 15Na$_2$O – 37.5B$_2$O$_3$ – 25P$_2$O$_5$ – 5.5ZnO – 2.0Cu</td>
<td>81.1</td>
<td>4.08</td>
</tr>
<tr>
<td>5</td>
<td>15Li$_2$O – 15Na$_2$O – 37.5B$_2$O$_3$ – 25P$_2$O$_5$ – 5.0ZnO – 2.5Cu</td>
<td>81.00</td>
<td>4.08</td>
</tr>
</tbody>
</table>
Table 2.2.9. For 15 Li₂O – 15 Na₂O – 37.5 B₂O₃ – 25 P₂O₅ – (7.5 – X) ZnO – x TiO₂ glass system.

<table>
<thead>
<tr>
<th>Sr No</th>
<th>Composition Li₂O – 15 Na₂O – 37.5 B₂O₃ – 25 P₂O₅ – (7.5 – X) ZnO – X TiO₂</th>
<th>Mole Wt. of Sample</th>
<th>Wt of raw material required for 30 gm Batch</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>81.44</td>
<td>Li₂CO₃</td>
</tr>
<tr>
<td>1</td>
<td>15Li₂O – 15Na₂O – 37.5B₂O₃ – 25P₂O₅ – 6.5ZnO – 1.0TiO₂</td>
<td></td>
<td>4.08</td>
</tr>
<tr>
<td>2</td>
<td>15Li₂O – 15Na₂O – 37.5B₂O₃ – 25P₂O₅ – 6.0ZnO – 1.5TiO₂</td>
<td></td>
<td>4.08</td>
</tr>
<tr>
<td>3</td>
<td>15Li₂O – 15Na₂O – 37.5B₂O₃ – 25P₂O₅ – 5.5ZnO – 2.0TiO₂</td>
<td></td>
<td>4.08</td>
</tr>
<tr>
<td>4</td>
<td>15Li₂O – 15Na₂O – 37.5B₂O₃ – 25P₂O₅ – 5.0ZnO – 2.5TiO₂</td>
<td></td>
<td>4.08</td>
</tr>
<tr>
<td>5</td>
<td>15Li₂O – 15Na₂O – 37.5B₂O₃ – 25P₂O₅ – 4.5ZnO – 3.0TiO₂</td>
<td></td>
<td>4.08</td>
</tr>
</tbody>
</table>

2.2.4 Batch Melting – (Melt-quenching)

The mixed charge was taken in alumina crucible. The 99.9% purity recrystallized 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 900°C continuously and up to 1100°C for 2 hrs. The crucible was heated to attain temperature 900-1100°C.
Fining and homogenization of melts

The molten glass was soaked at 1100°C for 2 hrs to achieve the good homogenized melt.

Casting: (Quenching)

After refining of the glass melt, the melt was air quenched on a previously polished hot stainless steel plate and processed immediately for annealing.

![Muffle Furnace Set Up](image)

**Fig.2.2.4.1. Muffle Furnace Set Up**

Annealing

When the molten glass is quenched, it develops lot of stresses. The process called annealing can nullify these stresses. The glass was annealed below the glass transition temperature for about 4 hrs to remove the stresses and obtain a stress free glass. For this purpose a precise temperature control furnace was used.

Wafering of glass

For various studies and characterizations, the glass samples are required in regular geometrical shapes. Therefore, the prepared glass is cut in different shapes and sizes using a precision cutting machine (Buehler Iso Met 4000). The sliced glasses were finished by means of polishing. The polishing was done using different grades of polishing papers.
The overall process for the glass melting is summarized in the flow chart 2.2.4.2.

**Fig.2.2.4.2. Flow chart for the glass melting procedure**
2.3 Characterization

The qualitative and quantitative analysis carried out to investigate various physicochemical aspects of the glass samples is described herein.

2.3.1 Density Measurement

Win Kelman and Ann Scott[2] proved that the additive calculation of glass density is possible by multiplication of a suitable factor of various oxide percentages in the glass. Hence, the glass is a mixture of the constituent oxides. The density is in close connection with the volume.

Minami and Tanka[3] have calculated the molar volume and ion concentration in silver ion conducting glasses from the measured density. Calvo and Jordan[4] reviewed the observed density and proposed a structural model to explain the variation of density with composition. The density measurements were also used to find the oxygen packing density in oxide glasses.

Density is generally measured by the fluid displacement method depending on Archimedes principle.

According the Archimedes principle, the buoyancy equals the weight of the displaced fluid. Archimedes Principle using distilled water or toluene as the buoyant medium calculates the density of the glass samples. The density was obtained by employing the relation.

\[
\rho = \frac{w_a}{w_a - w_b} \times \rho'
\]  

(2.1)

Where, \( w_a \) is the weight of sample glass in air, \( w_b \) is the weight of sample glass in buoyant liquid. \( (w_a - w_b) \) is the buoyancy. \( \rho' \) is density of buoyant. All the measurements were made using a digital balance. In case sample reacts with water, a suitable inert liquid such as toluene, xylene etc. can be selected as the immersion liquid.

The molar volume of the samples can be calculated from the following expression.

\[
\text{Molar Volume (} V_m \text{)} = \frac{M}{\rho}
\]  

(2.2)

Where, \( \rho \) is the density of the sample and \( M \) is the molecular weight of the sample. In the present immersion fluid and the reported density values are the average of at least three independently measured values.

The density measurement set up as shown in figure 2.3.1.
2.3.2 X-ray Diffraction

X-Ray diffraction (XRD) technique has been an indispensable tool for structural studies of solids [5]. It gives a complete description of the structure such as the crystal system, space group, unit cell dimension, atomic coordinates and electron density distribution around them [6].

Undoubtedly the most important and useful technique in solid state chemistry, X-ray diffraction, has been in use since the early part of this century. Crystalline solids give diffraction patterns that have a number of sharp lines it is due to long-range order. Non-crystalline solids i.e. glasses, gels gives diffraction patterns that have a small number of very broad humps.

It helps to identify the structure, degree of crystallinity, unit cell parameter, crystallite size. A phase is assumed to be pure when the X-ray pattern matches with that of the reported one and some or all peak positions are differing with those of the reported structures in the case of new structures.
The present investigation of phase formation of the glass samples was performed on X-ray diffractometer model Rigaku Miniflex II Desktop. The glass sample was finely powdered using mechanical grinder and this powder was subjected for the XRD analysis. The XRD patterns were recorded in the 2\(^\theta\) range 20-80 degree with scanning rate 1\(^0\)/mint with a Cu-K\(\alpha\) X-ray diffractometer as shown in figure 2.3.2.

### 2.3.3 UV-Visible Spectroscopy

The UV-VIS spectroscopy known to be a very sensitive and useful technique for the identification and characterization of the metal ion co-ordination and its existence in the framework or extra framework position of metal containing molecular sieves. There are two classes of spectra, namely emission and absorption spectra. An emission spectrum is obtained by analyzing the light emitted by a luminous source. An absorption spectrum is obtained by the spectroscopic analysis of the light transmitted by an absorbing medium which is placed between the light source and the detector. The present optical characterization of the samples was done using Shimadzu UV-3600-Vis-Nir Spectrophotometer is shown in fig 2.3.3. The glass discs were subjected to optical characterization at various stages i.e. the as it is annealed glass sample, strikes glass samples without fine polishing and after the fine polishing. The base line correction was done using air as reference medium and then only the
actual measurement was done. The parameters like dependence of % transmittance on composition and striking temperature were determined using the data obtained from optical analysis.

Fig. 2.3.3. UV-Spectrophotometer (Shimadzu UV-3600)

2.3.4 TGA - DTA

Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) were performed on a Shimadzu DTG 60 simultaneous instrument from 0.00 to 800°C as shown in fig 2.3.4.

Understanding of the solid state forms becomes more difficult when individual samples present as mixed forms [7].
The thermal analysis of the very finely polished (powder) glass samples was done using Dilatometer (Model Shimadzu DTG 60 TGA-DTA). The heating rate was kept to 40°C/min for all measurements. The properties like glass transition temperature, crystallization temperature were determined by using the above instrument.

2.3.5 FT-IR Analysis

The samples were subjected to the Fourier Transform infrared spectroscopic analysis to get the information on stretching modes of metal-oxygen groups. The FTIR utilizes a radiation source directed through an interferometer. Fourier Transformation Infrared Spectroscopy uses Michelson interferometer to produce an interferogram. The interferogram is related to IR spectrum by the mathematical operation, the Fourier transformation. The fundamental part of the instrument is the so-called Michelson interferometer [8]. The Alpha-Alpha FTIR Spectrophotometer-Bruker Model was used for the above analysis is shown in figure 2.3.5. The glass crushed in fine powder form and then mixed with KBr using agate mortar to get a fine homogeneous mixture of small particle size. The mixtures of fine powders are used for recording the IR spectra.
2.3.6 Micro Hardness

Glass samples were measured by indentation technique using Vickers indenter on a microhardness tester (Reichart Austria sr.no.363798) at room temperature is shown in fig 2.3.6. Before measurements, sample was polished with two parallel faces and then put on the tester. Indentation is obtained by applying 20g load for 30s and then the hardness of glass samples reported in GPa.

Smith and Sandland the UK developed an indentation test that employed a square-based pyramidal indenter made from diamond in 1925 [9].
2.3.7 Refractive Index

Refractive index is an important property for optical uses of glass. This is an important property because it is vital to the optical glasses used in the burgeoning photonics company. The various glass compositions were measured using a simple technique. The first laboratory refractometers sold commercially were developed by Ernst Abbe in the late 19th century [10]. The refractive index measurement set up is shown in figure 2.3.7.
2.3.8 Chemical Degradation Measurements (Corrosion)

2.3.8.1 Sample Preparation

In the materials science literature, there is a wealth of information on glass degradation, most of which focuses on water diffusion in silicate networks \cite{11-18}.

The glass samples were cut in the form of cylindrical discs of 15-20 mm diameter and 2-4 mm thickness. The samples were cleaned with acetone, trichloroethylene and alcohol in ultrasonic water bath. The glass surfaces were also observed under optical microscope before exposing to the corrosion medium. The photographs of chemical degradation of different glasses are shown in photo image 2.3.1.
2.3.8.2 Methodology

Samples of known weight and calculated surface area were held in the sample holder such that both sides of the sample were exposed uniformly to the medium. The holder assembly was then immersed in the PVC bottle containing the medium. The PVC bottle was kept in the constant temperature water bath maintained at the appropriate temperature.

The weight of the glass samples was observed intermittently after 1 hrs to 6 hrs depending on the weight loss. The study was carried out in the temperature range of room temperature. The weight calculated using the following formula

\[ D = \frac{W_o - W_t}{A t} = \text{g/cm}^2 \quad (2.3.1) \]

Where \( W_o \) is the initial weight of the glass sample in air, \( W_t \) is the weight of glass sample after time \( t \), \( A \) the surface area and \( t \) the time of measurement.

2.3.9 Dielectric Properties and A.C. Conductivity Measurements

The dielectric properties and a.c. conductivity measure all glasses with varying frequency at room temperature using LCR-Q meter (Model HIOKI3532-50 LCR Hi-Tester) in the frequency range 100 Hz to 5MHz with accuracy 0.001Hz. The glass
samples were characterized by using a.c. conductivity, real and imaginary part of impedance measure.

The A.C. conductivity of the prepared samples was calculated by using impedance analyser[19]. A.C. conductivity is one of the studies done on solids in order to characterize the bulk resistance of the crystalline sample.

The impedance analyser (HIOKI3532-50 LCR Hi- Tester) set up is shown in figure 2.3.8.

Fig.2.3.8. Impedence Analyzer (HIOKI3532-50 LCR Hi- Tester)
References: