Chapter 4

Physicochemical properties of cesium borosilicate glasses containing TiO$_2$
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4.1 Introduction

Development of borosilicate glass was first recorded in the late 19$^{th}$ century by German glassmaker Otto Schott and it was sold in Europe under the brand name "Duran" in 1893. In 1915, Corning glass works introduced Pyrex, a synonym for borosilicate glass. Thereafter rapid development has been noticed and quickly it became a ubiquitous material. The main reason behind this is that the borosilicate glass has a very low thermal expansion coefficient (3.3 x $10^{-6}$/K), about one-third that of ordinary glass and high chemical resistance properties, leading to the widely use of borosilicate glass for kitchen glassware, thermometer glass and railroad lanterns and now in diverse fields including optical glass, glass to metal seal, etc.$^{93, 94}$. However a scientific understanding of the glass network and its properties began only in early 1950. In 1955, Canadian scientists first experimentally established that HLW could be immobilized in glass.$^{95}$ This was followed by development of borosilicate matrix in UK (Fingal process) for vitrification of HLW.$^{96}$ In 1965, work on vitrification of HLW was started in India with emphasis on design and development of waste glass formulation and study of its properties including phase transformation, mechanical properties, radiation effects, chemical durability and volatilization.$^{97}$ A historical overview of the waste form development programme in nine countries including India was reviewed by Lutze and Ewing.$^{98}$ This highlights the fact that borosilicate glass has received the greatest attention in large scale immobilization of high level because of its excellent capabilities to accommodate almost all the elements of periodic table leading to a permanent and irreversible fixation of the nuclides in the
vitreous matrix. Additionally, glass being a solid solution is not susceptible to inter-granular corrosion.

In spite of these proven facts, borosilicate glass has not been considered for the preparation of $^{137}$Cs based radiation sources. Such glasses are very simple as compared to the nuclear waste bearing glasses, as it will not have other fission products and actinides. It could be simple borosilicate glass containing a very few or no other additives. The basic differences in both the glasses are in terms of total alkali oxides content. The alkali oxide loading in the Cs glass should be significantly higher to meet the specific activity requirements. It is known that chemical durability of the borosilicate glasses decreases with the increase of alkali oxide loading. Further, volatilization of the Cs in preparation of such glasses is one of the major concerns. Taking inferences from nuclear waste glass development, it can be stated that the incorporation of various additives do play a major role in optimizing the properties of the glasses.

At the beginning of the work therefore feasibility of using simple alkali borosilicate glass was examined. The loading of alkali oxide in glass was fixed at 20 mol% including 2.5 mol% Cs$_2$O while the rest was Na$_2$O. Loading of 2.5 mol% Cs$_2$O is the minimum requirement for use of this glass as a radiation source in medical irradiators. A minimum amount Na$_2$O is necessary to make the glasses at relatively lower temperature. In the present context it is assumed that the preparation of the glasses will be carried out using the recovered Cs solution containing equal amount of Na and Cs (as shown in Table 3-11). This will correspond to the stated loading of Na$_2$O while incorporation of 2.5 mol% Cs$_2$O.

In order to improve the properties of the glasses, incorporation of some additives in small quantities can be considered essential. A number of studies have been carried out in this
regards which have made it clear that the various additives played different roles in the glass network. Table 4-1 summarizes the effects of some additives on the change of properties of the resultant glasses. In this chapter, the influence of TiO$_2$ on the Cs borosilicate glass is illustrated by evaluating physiochemical properties of the glasses incorporated with different amount of TiO$_2$. Physico-chemical properties like density, molar volume, glass transition temperature, chemical durability and Cs-volatilization behavior were evaluated as a function of TiO$_2$ concentration. In addition, the structural aspects of these glasses were also investigated using FTIR, $^{11}$B MAS NMR spectroscopy and uv-visible spectro-photometry with a view to understand the role of TiO$_2$ on the physico-chemical properties of the glasses.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formation temp.</th>
<th>Durability</th>
<th>Cs-loss (Volatilization)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td></td>
<td>$\uparrow$</td>
<td>$\uparrow$</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td></td>
<td>$\uparrow$</td>
<td>$\downarrow$</td>
</tr>
<tr>
<td>MnO</td>
<td></td>
<td>$\downarrow$</td>
<td>$\uparrow$</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td></td>
<td>$\uparrow$</td>
<td>$\downarrow$</td>
</tr>
<tr>
<td>ZnO</td>
<td></td>
<td>$\uparrow$</td>
<td>$\uparrow$</td>
</tr>
</tbody>
</table>

### 4.2 Glass forming region of Na borosilicate system

Although sodium borosilicate glass can be obtained over a wide range of compositions as can be seen from the ternary diagram (Fig.4-1) representing glass forming region of the system, highlighting approximate compositional ranges of two commercial glass families viz., Vycor glasses (area enclosed in magenta) and Pyrex type glasses (yellow shaded area), a
limited region (SiO$_2$: 35-65, B$_2$O$_3$:10-20 and Na$_2$O:10-20, waste oxide: 15-30) has been used for the production of base glass for nuclear waste immobilization (area covered by black crossed lines)$^{98}$. The glass forming region of interest in the present study is shown as circle filled in dark cyan color.

Figure 4-1: Ternary diagram of sodium borosilicate glass highlighting region of interest of some important class of glasses

4.3 Preparation of alkali borosilicate glasses

The characteristics of the simplified alkali borosilicate glasses prepared as per the formulation, 10 Cs$_2$O + 15 Na$_2$O + (75-x) SiO$_2$ + x B$_2$O$_3$, ‘x’ varied from 25-45 w% is shown in Table 4-2. It can be seen on the Table that the borosilicate glass containing ≥ 50 wt% of SiO$_2$ has pour temperature above 950°C. The chemical durability of the glasses in the series, as expected, are found to increase with the increase of SiO$_2$ concentration. From these results, it is
clear that among the stated glasses that has low pouring temperature and Cs leach rate, #CBS-3 is the formulation considered as a baseline formulation for further investigations. Hereafter, it will be referred to as “base glass”.

Table 4-2: Characteristics of the Cs-borosilicate glasses prepared as per formulation (wt %)

\[
10 \text{Cs}_2\text{O} + 15 \text{Na}_2\text{O} + (75-x) \text{SiO}_2 + x \text{B}_2\text{O}_3
\]

<table>
<thead>
<tr>
<th>Batch No.</th>
<th>SiO\textsubscript{2} (wt%)</th>
<th>B\textsubscript{2}O\textsubscript{3} (wt%)</th>
<th>Pour temp. (°C)</th>
<th>Density (g/cm\textsuperscript{3})</th>
<th>Leach rate (g/cm\textsuperscript{2}/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Na</td>
</tr>
<tr>
<td>CBS-1</td>
<td>50</td>
<td>25</td>
<td>&gt; 950</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CBS-2</td>
<td>45</td>
<td>30</td>
<td>950</td>
<td>2.46</td>
<td>1.7 x 10\textsuperscript{-3}</td>
</tr>
<tr>
<td>CBS-3</td>
<td>40</td>
<td>35</td>
<td>900</td>
<td>2.47</td>
<td>3.0 x 10\textsuperscript{-3}</td>
</tr>
<tr>
<td>CBS-4</td>
<td>35</td>
<td>40</td>
<td>900</td>
<td>2.48</td>
<td>3.8 x 10\textsuperscript{-3}</td>
</tr>
<tr>
<td>CBS-5</td>
<td>30</td>
<td>45</td>
<td>900</td>
<td>2.49</td>
<td>4.0 x 10\textsuperscript{-3}</td>
</tr>
</tbody>
</table>

### 4.4 Preparation of TiO\textsubscript{2} containing glasses

As mentioned above, the major thrust of this study is to improve the properties of the baseline glass by incorporating TiO\textsubscript{2}. The additive can be incorporated in the glass either at the expense of B\textsubscript{2}O\textsubscript{3} or SiO\textsubscript{2}. In order to select the suitable one between the two alternatives, glasses were prepared adopting both the approaches and characterized (Table 4-3). Elemental (Na, Cs) leach rate for the glass (Ti-10A), prepared by incorporation of TiO\textsubscript{2} (10 mole %) at the expense of SiO\textsubscript{2}, is found to be an order of magnitude higher than the base glass. Higher concentration of Si in leachate, however, indicates that the network dissolution also take place during leaching. It is known that SiO\textsubscript{2} decrease has a negative effect and TiO\textsubscript{2} increase has a positive effect on chemical durability\textsuperscript{99}. The result clearly indicates that effect of SiO\textsubscript{2} is more...
dominant than TiO$_2$. On the other hand, the glasses prepared by incorporation of TiO$_2$ (10 mole%) with decrease of B$_2$O$_3$ showed higher chemical durability as compared to the base glass. Based on these results, the approach of incorporation of TiO$_2$ at the expense of B$_2$O$_3$ was selected and followed throughout the work. Five glasses of this series of molecular formula (SiO$_2$)$_{0.4}$ (B$_2$O$_3$)$_{0.35-x}$ (Na$_2$O)$_{0.175}$ (Cs$_2$O)$_{0.025}$ (TiO$_2$)$_x$, where x =0, 2.5, 5, 7.5 and 10, have been prepared and characterized as discussed below.

Table 4-3: Characteristics of the Cs-borosilicate glasses prepared from base glass by incorporating TiO$_2$

<table>
<thead>
<tr>
<th>Batch No</th>
<th>Batch composition (mole%)</th>
<th>Leach rate (g/cm$^2$/d)</th>
<th>pH of leachate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO$_2$</td>
<td>B$_2$O$_3$</td>
<td>Na$_2$O</td>
</tr>
<tr>
<td>Base glass</td>
<td>45</td>
<td>35</td>
<td>17.5</td>
</tr>
<tr>
<td>Ti-10</td>
<td>45</td>
<td>25</td>
<td>17.5</td>
</tr>
<tr>
<td>Ti-10A</td>
<td>35</td>
<td>35</td>
<td>17.5</td>
</tr>
</tbody>
</table>

4.5 Chemical analysis of glass

The chemical analysis of the glasses was performed as per the procedure discussed in section 2.5.2. Experimentally determined concentrations of Na and Cs in the glasses were shown in Table 4-4. The error (standard deviation) associated with loss in wt % calculation for both the elements were found to be ± 2%. It is clear from Table 4-4 that both Na and Cs loss for ‘base glass’ is higher than all other glasses (Ti-2.5 to Ti-10). Among the four TiO$_2$ containing glasses, minimum loss for both Cs and Na was observed for the glass containing 5 mole% of TiO$_2$. Further, these results confirmed that 94% or more of both Na and Cs are
present in all the glasses. Although other constituents in glass were not analyzed, it can be reasonably assumed that loss of boron will be lower than that of Cs. The Si and Ti content are assumed to be the same as batch composition.

<table>
<thead>
<tr>
<th>Batch No</th>
<th>Na&lt;sub&gt;2&lt;/sub&gt;O</th>
<th>Cs&lt;sub&gt;2&lt;/sub&gt;O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated</td>
<td>Expt.</td>
</tr>
<tr>
<td>‘base glass’</td>
<td>15.39</td>
<td>14.36</td>
</tr>
<tr>
<td>Ti-2.5</td>
<td>15.33</td>
<td>14.77</td>
</tr>
<tr>
<td>Ti-5.0</td>
<td>15.26</td>
<td>14.88</td>
</tr>
<tr>
<td>Ti-7.5</td>
<td>15.20</td>
<td>14.71</td>
</tr>
<tr>
<td>Ti-10</td>
<td>15.14</td>
<td>14.20</td>
</tr>
</tbody>
</table>

### 4.6 General characteristics of the glasses containing TiO<sub>2</sub>

#### 4.6.1 Density and molar volume

Density of the glass samples were determined as per the procedure described in section 2.6. The measured density (g/cm<sup>3</sup>) and calculated molecular weight (g) from batch composition of the glasses were used to calculate the molar volume (cm<sup>3</sup>) of the glasses by using the following equation:

\[
\text{Molar volume} = \frac{\text{Molecular weight}}{\text{density}}
\]

Fig.4-2 shows the measured density and calculated molar volume of the glasses containing varying concentration of TiO<sub>2</sub>. Density of the glasses was found to be similar within
the limit of experimental error. The molar volume was also found to be almost same (27.5±0.3 cm³).

![Graph showing density and molar volume of glasses](image)

**Figure 4-2:** Density and molar volume of the Cs borosilicate glasses ((SiO₂)₀.₄ (B₂O₃)₀.₃₅₋ₓ (Na₂O)₀.₁₇₅ (Cs₂O)₀.₀₂₅ (TiO₂)ₓ) containing different concentration of TiO₂.

### 4.6.2 XRD analysis

XRD patterns of the glass samples recorded with an X-ray diffractometer which uses CuKα radiation are shown in Fig.4-3. All the patterns showed a broad peak around a 2θ value...
Figure 4-3: XRD profiles of the Cs borosilicate glasses of general formula $(\text{SiO}_2)_{0.45} (\text{B}_2\text{O}_3)_{0.35-x} (\text{Na}_2\text{O})_{0.175} (\text{Cs}_2\text{O})_{0.025} (\text{TiO}_2)_x$ with $x$ varying from 0.0 to 10.0 of $25^\circ$, characteristic of the amorphous borosilicate network. Absence of sharp peaks clearly confirmed that no crystalline phases (within the detection limits of XRD technique) are present in these glasses.

### 4.6.3 Glass transition temperature

Glass transition temperature was determined from the onset of the first endothermic peak of DTA curve (Fig.4-4) generated at a heating rate of $10^\circ\text{C/min}$ using setaram make TG-DTA instrument (section 2.9.4.2). The glass transition temperature of all the glass samples has been plotted as a function of TiO$_2$ concentration and is shown in Fig.4-5. It is found that the glass transition temperature decreases systematically with increase of TiO$_2$ concentration in glass. The observed variation can be explained based on the bond energy values of B-O and Ti-O bonds$^{101}$. As the bond energy values are lower for Ti-O bonds compared to B-O bonds, replacement of B-O bonds by Ti-O bonds results in the decrease of average bond energy of the glass network, leading to reduction in glass transition temperature.
Figure 4-4: TG-DTA profile for the Cs-borosilicate glass containing 7.5 mole% TiO$_2$ (Batch No. Ti-7.5)

Figure 4-5: Glass transition temperature of Cs-borosilicate glasses containing varying amount of TiO$_2$, line is guided to eye

4.6.4 Chemical durability

Chemical durability is the property symbolizing the extent of resistance against hydrolytic attack and depends mainly on the nature of the constituents and their relative
concentrations in glass\textsuperscript{102, 103, 104, 105}. It is generally measured by conducting leaching tests. In
the present study, leaching tests were performed as per the procedure described in section.2.7 for comparative evaluation of formulation. In brief, 1.0 g glass sample (-100+200 mesh ASTM) and 10 cm\textsuperscript{3} of ultrapure water was heated in air-oven at 90\degree C for 24 hours, and the measured concentrations of Na, Cs, and Si in leachate were used to judge the chemical durability of the glasses. The normalized elemental leach rate of the glasses as a function of TiO\textsubscript{2} content is shown in Fig.4-6.

![Figure 4-6: Leaching of Na and Cs from Cs-borosilicate glasses in distilled water at 90\degree C for 24 hours, lines are guided to eye, general formula of the glasses: \((\text{SiO}_2)_{0.4} (\text{B}_2\text{O}_3)_{0.35-x} (\text{Na}_2\text{O})_{0.175} (\text{Cs}_2\text{O})_{0.025} (\text{TiO}_2)_x\) ](image)

The measured pH of leachate for the glasses was found to be within 9.35 to 9.10, highest for ‘base glass’, lowest for Ti-10 and almost same (9.20-9.25) for the other three glasses. The leach rate of Na, Cs and Si are found to be in the order: Na>Cs>Si. In detail, the Si
concentration in the leachate for all the glasses is found to be almost same, and this has been attributed to the fact that network dissolution took place to the same extent for all the glasses during the course of leaching. Leaching pattern of Na and Cs can be explained by considering ion exchange reaction of glass and hydronium ions in which diffusion is the rate controlling step. As \( \text{Na}^+ \) ion has a smaller ionic radius compared to \( \text{Cs}^+ \) ion, \( \text{Na}^+ \) ions have higher diffusion coefficient and mobility compared to Cs ions in the same glass matrix. This accounts for the increased leach rate of Na ions as compared to Cs ions from glass. In totality, the chemical durability of the glasses (with respect to Cs and Na leach rate) improved significantly due to incorporation of TiO\(_2\) at the expenses of B\(_2\)O\(_3\). This overall improvement of chemical durability is due to a combined effect of both TiO\(_2\) increase and B\(_2\)O\(_3\) decrease, as both factors are well known to improve the matrix durability. More specifically, it can be noted that the improvement of chemical durability with respect to Cs leach rate is more noticeable than Na. For example, the Cs leach rate was found to decrease almost linearly with increase of TiO\(_2\) concentration and about 15 times lower Cs leach rate was noted for the Ti-10 glass (containing 10 mole\% TiO\(_2\)) compared to the glass containing no TiO\(_2\) (‘base glass’). On the other hand, no improvement on Na leach rate, due to the presence of TiO\(_2\) up to 7.5 mole\%, was observed. The preferential leach rate of Na and Cs may possibly be due to the structural modification brought about by TiO\(_2\) incorporation in the glass at the expense of B\(_2\)O\(_3\). This aspect has been investigated in detail and is described in a later section of this chapter.

### 4.7 Volatilization of Cs

A large number of studies pertaining to the effect of TiO\(_2\) on volatilization of Cs have been reported from various laboratories and the observations can be summarized as follows. Rastogi et al\(^{107}\) reported that volatility of Cs can be reduced by using a little amount of TiO\(_2\),
possibly due to the formation of thermally stable compounds such as Cs$_2$O-4TiO$_2$. The effect of TiO$_2$ on reduction of Cs-volatility was also observed by Kelly et al. during the preparation of glass from zeolite$^{108}$. On the other hand, Gray$^{109}$ has shown that addition of TiO$_2$ in zinc borosilicate matrix increases the volatility of Cs. About 11% of Cs was found to be volatilized when 12 wt% TiO$_2$ was added to 76-183 glass. In 1981, Saidl et al. reported that the use of TiO$_2$ in borosilicate glass lowers Cs volatility$^{110}$. It is to be noted that all the above studies have been carried out in connection with the incorporation of nuclear waste and no data for only Cs bearing borosilicate glasses are reported till date, to the best of authors’ knowledge. Based on the above discussion it is clear that the role of TiO$_2$ in the extent of Cs losses due to volatilization is significantly dependent on the matrix composition. Hence, a systematic study on the extent of Cs-volatilization as a function of TiO$_2$ content in glass was performed.

In the present study, as described in section 2.8, different approaches were made to measure the extent of Cs volatilization as well as to provide an understanding on the volatilization behavior of Cs from borosilicate glasses as a function of TiO$_2$ content and the results are discussed below.

(a) Measurement of Cs volatilization loss in glass making

This method (described in section 2.8.1) in principle is a direct approach, as glass forming mixture is heated and the evolved glasses were collected and analyzed chemically. It is important that sample of evolved gas should have a measurable amount of volatilized species, so that a statistically reliable chemical analysis could be performed. In general, volatilization study with more glass (with higher batch size) generates a measurable amount of species. Otherwise, accuracy in analytical results can be improved by using radiotracer technique. In this method, as batch size used was 2 g glass, radiotracer technique was used. In addition, Cs
analysis was performed after dissolving the glass sample in 40% HF and the analysis results was used to ascertain the material balance. For some selected batches, detailed elemental analysis in solutions of volatilized products was also carried out.

Table 4-5 shows the results of the extent of Cs volatilization during the glass formation. It can be seen that a maximum of about 4% of Cs was volatilized in the sample containing no TiO₂ (‘base glass’). The loss of Cs was found to reduce from 4% to 1.5% (about 60% reduction) with the incorporation of 2.5 mole% of TiO₂. A further marginal decrease in Cs-loss was noted for the batch containing 5 mole% of TiO₂ and thereafter a trend reversal was observed. The loss of Cs was found to be about 2.8% for the last two batches containing 7.5 and 10 mole% of TiO₂. As compared to the base glass, all the batches with TiO₂ showed lower loss of Cs. A similar conclusion can also be arrived from the Cs concentrations in dissolved glass solution. The trend of Cs volatilization values obtained here compares to Table 4.4.

Table 4-5: Distribution of Cs in vapor and glass during formation of the Cs-borosilicate glasses

<table>
<thead>
<tr>
<th>Batch No</th>
<th>Concentration of Cs (%)</th>
<th>No. of tests</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dissolved glass (a)</td>
<td>Scrub solution (b)</td>
</tr>
<tr>
<td>‘Base glass’</td>
<td>95.95-96.15</td>
<td>3.55-3.99</td>
</tr>
<tr>
<td>Ti-2.5</td>
<td>97.92-98.81</td>
<td>1.53-1.55</td>
</tr>
<tr>
<td>Ti-5.0</td>
<td>96.27-97.84</td>
<td>1.39-1.48</td>
</tr>
<tr>
<td>Ti-7.5</td>
<td>96.76-97.55</td>
<td>1.93-2.80</td>
</tr>
<tr>
<td>Ti-10.0</td>
<td>96.21-96.35</td>
<td>2.64-2.82</td>
</tr>
</tbody>
</table>
The higher losses incurred in as melted glasses is possibly due to exposure of the glasses to elevated temperature for pouring. It is worth mentioning that more than 90% of the total Cs present in scrub-solution was obtained from the washing of the silica tube and a little amount was in the 1st bubbler (section 2.8.2). The Cs present in the 2nd bubbler was negligible and therefore it can be stated that no Cs escaped from the system. For all the tests, good mass balance of Cs was obtained, as it can be seen that > 99% of Cs was accounted for.

Result of detailed chemical analysis of the solutions generated from washing of the volatilization set-up is shown in Table 4-6. It can be seen that the volatilization loss of boron species is more significant after Cs. This also confirmed that Na is the least volatile element as compared to B and Cs and its volatilization loss for the glasses under investigation was found to be more or less same. Volatilization profile of B species was found to follow similar trend as described above for Cs.

Table 4-6: Elemental composition of the scrub solutions (in ppm) analyzed by ion chromatography

<table>
<thead>
<tr>
<th>Batch No</th>
<th>Na</th>
<th>Cs</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base glass</td>
<td>3.3</td>
<td>31.5</td>
<td>10.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(32.7*)</td>
<td></td>
</tr>
<tr>
<td>Ti-5.0</td>
<td>4.4</td>
<td>9.2</td>
<td>8.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(11.2*)</td>
<td></td>
</tr>
<tr>
<td>Ti-10.0</td>
<td>4.6</td>
<td>20.7</td>
<td>14.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(21.5*)</td>
<td></td>
</tr>
</tbody>
</table>

* calculated from the radiometric measurement of $^{137}$Cs activity in solution (i) before and (ii) after glass formation and (iii) initial concentration of Cs in solution taken for glass making.

# analyzed using ICP-AES.
(a) Measurement of Cs volatilization by thermogravimetry method

As this method is highly sensitive with regard to the change of weight due to heating, it was used to study the Cs volatilization from preformed glasses. In this analysis, about 40 mg of glass sample in platinum crucible was heated under static air to 900°C at the heating rate of 10°C/min and then isothermal heating was continued at 900°C for 2 hours, using a Setaram make TG-DTA instrument. TG-DTA profile, corresponding to the glass sample containing 7.5 mole% TiO₂, is shown in Fig.4-4. It can be seen that a little weight gain was observed during the 1st heating sequence i.e., from 100-900°C and thereafter constant weight was recorded throughout the heating period (2 hours) at 900°C. The observations are in accordance with the results of volatility tests from simulated high level waste glass, reported by J. Harbour. The experimentally observed TG-DTA profile for all the glasses under investigation was found to follow a similar pattern as shown in Fig.4-4. Based on these results, it is inferred that no loss of Cs, to the level of sensitivity of TG-DTA instrument, occurred from the preformed glasses.

(c) Chemical analysis method

It was seen that thermogravimetry method, though very sensitive, did not yield any information about weight losses possibly due to very low quantity of the sample and lower experimental temperature. In the present study, therefore, higher quantity of sample was used and the volatile component was dissolved and analyzed chemically. As mentioned earlier, the heating of preformed glass is equivalent to soaking stage, which is the longest duration process in glass preparation and the glass at this stage endures minimum turbulence from froth formation/bubble evolution. The effect of temperature is more prominent at this stage, hence Cs volatilization loss in this period was measured and used as a representative parameter for
comparing the effect of composition. In this study, preformed glass (batch size: 25 g) was
heated for about 6 hours per day for 4 days and the amount of Cs volatilized during 6 hours of
heating was obtained by analyzing the solutions obtained from washing the whole setup where
Cs was deposited (section 2.8.2.2). Volatilization profile for two glass samples, viz., ‘base
glass’ and Ti-5, were determined at three different temperatures (i.e., 900, 950 and 1000°C).

The result of volatilization study is presented in terms of cumulative loss of Cs after 24
hours of heating in Table 4-7. It can be seen that the extent of Cs loss for both the glasses
heated at 900°C for 24 hours are very low and almost similar. However 950 and 1000°C heated
samples showed increasingly higher Cs losses. The influence of TiO₂ on suppressing Cs
volatility is clearly seen.

Table 4-7: Cumulative loss of Cs (mg/cm²) from the preformed Cs borosilicate glasses after 24
hours of heating at different temperatures

<table>
<thead>
<tr>
<th>Glass sample</th>
<th>Heating temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>900</td>
</tr>
<tr>
<td>Base glass</td>
<td>0.23</td>
</tr>
<tr>
<td>Ti-5</td>
<td>0.20</td>
</tr>
</tbody>
</table>

4.7.1 Discussion on Cs volatilization results

The loss of Cs due to volatilization during heating at elevated temperature may occur
through several mechanisms, depending upon the composition of the melt and temperature.
Thermal decomposition of CsNO₃ (taken as starting material for glass formation) takes place at
around 400-600°C, mainly through the following steps:\(^{112}\):
Hence it is reasonable to assume that volatilization loss of Cs starts at around 500°C and continues up to fusion temperature of the glass. Since Cs metal is highly reactive with air, and our experiments were carried out under constant air flow conditions, it is quite possible that majority of the Cs can get converted to Cs(OH), which is the most volatile among all Cs compounds\textsuperscript{113}. In addition, some amount of Cs may volatilize in the form of Cs\(_2\)(BO\(_2\))\(_2\) (g), Cs(BO\(_2\)) (g), as reported by Asano et al\textsuperscript{114}.

From the elemental composition profile of the scrub solution (Table 4-6), it can be inferred that some such compounds may form during formation of all the glasses under investigation. Some loss of Cs is also expected during soaking of the glass at 900°C for homogenization. The values in Table 4-5 represent the cumulative loss of Cs in glass making, starting from the decomposition of raw materials including soaking at 900°C for 2 hours. According to the results of Rudolph et al., the presence of B\(_2\)O\(_3\) or TiO\(_2\) in the melt is known to reduce Cs volatilization and the TiO\(_2\) has been found to show pronounced effect compared to B\(_2\)O\(_3\) in reducing the extent of Cs volatilization\textsuperscript{115}. Hence in the present study, as TiO\(_2\) is incorporated at the expense of B\(_2\)O\(_3\), it is reasonable to conclude that the presence of TiO\(_2\) is responsible for the decrease in the extent of Cs volatilization. Furthermore, the peculiar variation of Cs losses as a function of TiO\(_2\) content in the glasses may possibly be due to the difference in the nature of interaction of Ti\(^{4+}\) ions with glass constituents, as TiO\(_2\) is known to behave as a network former and modifier depending upon its concentration in the glass\textsuperscript{116}. This
information can be obtained by investigating the structural aspects of the glasses and the same has been described in the latter section of this chapter.

Further volatilization behavior of Cs at three different temperatures is presented in Figs. 4-7 and 4-8 in the form of cumulative Cs loss against square root of heating time. It can be considered that the nature of loss rate profile is a reflection of processes involved in volatilization. Elemental volatilization from glass melt, as in the case of present study in which all the glasses are in molten state at 900°C and above, occurred vide processes like (i) diffusion of Cs through the melt to surface, (ii) transport through melt/vapor interface and (iii) transport in the atmosphere\textsuperscript{[117]}. It is therefore reasonable to assume that the volatilization profiles in Figs. 4-7 and 4-8 give an average picture of all the processes involved with the characteristic features of the rate controlling processes. For example, only one slope in rate loss profiles suggests that volatilization occurred predominantly through one type rate determining process. From the straight-line plots of cumulative Cs losses against square root of time, it can be stated that volatilization of Cs occurred predominantly through diffusion controlled process and the same can be expressed by equation 1 below\textsuperscript{[76]}:

\[ Q = C_0 \cdot \sqrt{\frac{D}{\pi}} \cdot \sqrt{t} \]  \hspace{1cm} \text{...(15)}

In equation 1, \( Q \) (mg/cm\(^2\)) represents the amount of Cs diffused from melt of unit surface area after \( t \) (h) time, \( C_0 \) (mg/cm\(^3\)) is the initial concentration of Cs in melt and \( D \) (cm\(^2\)/h) is diffusion coefficient (the quantity of material diffused through a unit area in unit time under a unit concentration gradient). Assuming negligible Cs loss takes place during glass preparation, the values of \( C_0 \) can be obtained from the measured density of the glasses and amount of Cs added in glass preparation. From the \( C_0 \) values and slope of the straight line plots (Figs 4-7 & 4-8), the
values of diffusion coefficient were evaluated for all the glasses heated at different
temperatures. As diffusion is a temperature dependent phenomenon, diffusion coefficient at any
temperature can be expressed by the following equation:\(^{118}\):

\[ D = D_0 \cdot e^{-\frac{E}{RT}} \]  

where \( R \) is universal gas constant and \( T \) is the absolute temperature. Calculated \( D \) values of the
glasses are plotted as a function of \( 1/T \) and are shown in Fig.4-9. From the slope and the
intercept of each line, the values of activation energy, \( E \) and \( D_0 \) for Cs diffusion from the
glasses have been calculated (Table 4-8). The activation energy values for ‘base glass’ and Ti-5
glass were as found to be 513 and 360 kJ/mol, respectively. Interestingly, Cs loss is lower for
Ti-5 glass even though the activation energy for Cs diffusion is lower than ‘base glass’. Similar
trend in weight loss and activation energy has also been reported for borosilicate glasses having
different compositions by various authors\(^{76,119}\). The calculation of \( D_0 \) value for these glasses
(‘base glass’ and Ti-5) showed that their differences are quite significant, \( (3.49 \times 10^{12} \text{ cm}^2/\text{s} \) for
‘base glass’ and \( 4.73 \times 10^5 \text{ cm}^2/\text{s} \) for Ti-5) and control Cs loss.
Figure 4-7: Cs loss profile as a function of square root of heating time for glass sample of molecular formula \((\text{SiO}_2)_{0.45} (\text{B}_2\text{O}_3)_{0.35} (\text{Na}_2\text{O})_{0.175} (\text{Cs}_2\text{O})_{0.025}\) in dry air at different temperature.

Table 4-8: Activation energy and pre exponential factor for Cs volatilization from the glasses

<table>
<thead>
<tr>
<th>(\text{M}_2\text{O}_x)</th>
<th>(E) (kJ/mol)</th>
<th>(D_0) (cm(^2)/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>‘base glass’</td>
<td>513</td>
<td>3.49 x 10(^{12})</td>
</tr>
<tr>
<td>Ti-5</td>
<td>359</td>
<td>4.73 x 10(^5)</td>
</tr>
</tbody>
</table>
Figure 4-8: Cs loss profile as a function of square root of heating time for glass sample of molecular formula \((\text{SiO}_2)_{0.45} (\text{B}_2\text{O}_3)_{0.30} (\text{Na}_2\text{O})_{0.175} (\text{Cs}_2\text{O})_{0.025} (\text{TiO}_2)_{0.05}\) in dry air at different temperature.

Figure 4-9: Plot of \(\ln(D)\) against \(1/T\) for the base glass and glass sample containing 5 mole% \(\text{TiO}_2\).
4.8 **Structural characterization of the glasses**

4.8.1 FTIR study

FTIR spectra of the glass sample was recorded from KBr pellets using a Fourier transform infrared (FT-IR) spectrometer (model: Jasco-660) with an average of 50 scan per spectrum at a resolution of 4 cm\(^{-1}\) are shown over the region of 440-2000 cm\(^{-1}\) in Fig.4-10. The glass sample without any TiO\(_2\) is characterized mainly by three peaks centered at 1408 cm\(^{-1}\), 987 cm\(^{-1}\) and 454 cm\(^{-1}\). The peak around 987 cm\(^{-1}\) also has a weak shoulder around 686 cm\(^{-1}\). The peak around 1408 cm\(^{-1}\) is attributed to the B-O stretching vibration of BO\(_3\) and BO\(_4\) structural units present in the glass\(^{120}\). The broad peak around 987 cm\(^{-1}\) and weak shoulder around 686 cm\(^{-1}\) have arisen due to the asymmetric and symmetric stretching vibrations of Si-O-Si/Si-O-B linkages, respectively\(^{121}\). The peak around 454 cm\(^{-1}\) has arisen due to the bending

![FTIR spectrum](image)

**Figure 4-10:** FTIR patterns of Cs-borosilicate glasses containing different amounts of TiO\(_2\) over the region of 400-2000 cm\(^{-1}\)
vibration of Si-O-Si/Si-O-B linkages. Similar IR patterns were also observed for glass samples with different TiO$_2$ contents. No additional peak characteristic of Ti-O vibrations has been observed in these patterns due to the low IR activity of Ti-O bonds compared to the Si-O or B-O bonds. It is worth mentioning that with the incorporation of TiO$_2$, the line shape corresponding to asymmetric stretching vibration has been found to change significantly, as can be seen from Fig.4-11. For 2.5 mole% TiO$_2$ incorporation in the glass, there is significant narrowing in the line shape corresponding to 987 cm$^{-1}$ peak (characteristic of Si-O-Si/Si-O-B asymmetric stretching vibration). Increase in TiO$_2$ content to 5 mole% resulted in further reduction of the line width of this peak. However for more than 5 mole% TiO$_2$ (i.e. for 7.5 and 10 mole% TiO$_2$) incorporation, line width began to increasing. The observed variations in the line width can be attributed to variation in the extent of strain/distortion associated with the borosilicate network with the addition of TiO$_2$. When a bridging oxygen atom gets converted to

![Figure 4-11: FTIR spectrum of Cs-borosilicate glasses containing different amounts of TiO$_2$ (normalized at peak 970-1010 cm$^{-1}$)](image-url)
non-bridging oxygen atom, the strain/distortion associated with the network decreases. This leads to decrease in line width of the IR absorption peak. However, above 5 mole% TiO₂, the line width increase has been attributed to the network forming action of TiO₂. The change in the behavior of TiO₂ from network modifier to network former is also reported by other investigators¹²².

4.8.2 NMR study

¹¹B MAS NMR patterns for the glass samples loaded with different amounts of TiO₂ are shown in Fig. 4-12. All the patterns are found to consist of less intense broad peaks around -3 ppm and sharp peak around -19 ppm along with side bands. Based on earlier ¹¹B MAS NMR studies¹²³, the sharp and broad peaks are respectively attributed to boron in tetrahedral (BO₄) and trigonal (BO₃) configurations. As ¹¹B is a quadrupolar nucleus (I = 3/2), boron in the trigonal coordination lacks cubic symmetry, and gives rise to a broad peak. Unlike this, cubic nature of the tetrahedrally coordinated boron structural units results in negligible quadrupolar coupling constant and thereby giving rise to a sharp NMR peak. The area under both the peaks was calculated and relative percentages of both BO₄ and BO₃ structural units have been determined and are given in Table 4-9. The relative concentrations of BO₄ structural units have been found to increase with the incorporation of 2.5 mole% TiO₂. However above 2.5 mole% TiO₂ incorporation, the relative concentration of BO₃ and BO₄ structural units remained more or less same. These results demonstrate that as TiO₂ content in the glass increases at the expense of B₂O₃ (upto 2.5 mole%), the boron network is affected initially. Further, the results prove that beyond 2.5 mole% TiO₂ incorporation the relative concentrations of BO₃ and BO₄ structural units are not responsible for the observed changes in the physical properties of the glass samples. With incorporation of TiO₂ up to 2.5 mole%, there exists a redistribution of the
cations in the borosilicate network. However, above 2.5 mole% TiO$_2$, Ti$^{4+}$ ions do not have any interaction with boron structural units as revealed by the identical values of the relative concentration of BO$_3$ and BO$_4$ structural units. This is possible if Ti$^{4+}$ ions interact with the silicon structural units present in the glass.

Figure 4-12: $^{11}$B MAS NMR profile of the glasses containing varying concentration of TiO$_2$

Table 4-9: Concentrations of BO$_4$ and BO$_3$ structural units in the Cs-borosilicate glasses containing different concentrations of TiO$_2$ determined from $^{11}$B MAS NMR profiles

<table>
<thead>
<tr>
<th>Batch No</th>
<th>Batch composition of B$_2$O$_3$ (mole%)</th>
<th>Relative concentration (%) in glass</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>BO$_4$</td>
</tr>
<tr>
<td>Ti-0</td>
<td>35.0</td>
<td>58</td>
</tr>
<tr>
<td>Ti-2.5</td>
<td>32.5</td>
<td>63</td>
</tr>
<tr>
<td>Ti-5.0</td>
<td>30.0</td>
<td>64</td>
</tr>
<tr>
<td>Ti-7.0</td>
<td>27.5</td>
<td>65</td>
</tr>
<tr>
<td>Ti-10.0</td>
<td>25.0</td>
<td>65</td>
</tr>
</tbody>
</table>
4.8.3 UV-Visible optical absorption study

Based on the FTIR and $^{11}$B MAS NMR studies it is inferred that the relative concentration of non-bridging oxygen atoms changes with increase in the concentration of TiO$_2$ at the expense of B$_2$O$_3$ in the glass. Such changes in the relative concentration of non-bridging oxygen atoms result in change in the $E_{\text{optical}}$ values of the glass samples, and this can be followed by recording the uv-visible optical absorption spectrum of the sample. UV-VIS spectra were recorded from 800 to 200 nm with a thin plate of glass using Jasco spectrophotometer, (Model V-650), at a rate of 400 nm/minute scanning speed (section 2.9.7).

Fig.4-13 shows the uv-visible optical absorption spectrum of three representative glass samples. All the absorption curves are characterized by a broad onset over the region of 360 - 325 nm, which is characteristic of the glassy nature of the sample$^{124}$. For glass sample without any TiO$_2$ (‘base glass’), the onset of absorption is found to be around 325 nm. With incorporation of TiO$_2$, the onset of absorption was found to get red shifted for all the samples.

![Image of UV-visible optical absorption spectra](image.png)

Figure 4-13: UV-visible optical absorption spectra of Cs borosilicate glasses containing different amounts of TiO$_2$. 
As the onsets of absorptions are quite broad, attempt was not made to exactly calculate the onset wavelength of absorption. However the absorption coefficient (α) in these glasses can be related to energy gaps (optical gaps) in the glass by the power law suggested by Davison and Mott\textsuperscript{125}, which can be expressed as

\[ αhν = A(E - hν)^r \]

where, A is a constant and r can have values 2, 3, ½ etc. For indirect transitions in glassy materials, value of r can be assumed to be 2. Hence in the plot of \((αhν)^{1/2}\) versus hν, known as extrapolation of the linear graph in the onset region to the x-axis can give the value of the optical gap in the glass. The Tauc plot (Fig.4-14) shows the variation of \((αhν)^{1/2}\) as a function of hν for the glasses. For glass sample without any TiO\textsubscript{2} content, the \(E_{\text{optical}}\) value is found to be 3.60 eV. Incorporation of 2.5 mole\% TiO\textsubscript{2} resulted in reduction in the \(E_{\text{optical}}\) value namely to 3.52 eV. Further reduction of \(E_{\text{optical}}\) value (3.42 eV) was noted for the glass containing 5.0 mole\% of TiO\textsubscript{2}. The \(E_{\text{optical}}\) values for the glasses containing 7.5 and 10 mole\% TiO\textsubscript{2}, are comparable with that of the glass sample with 5 mole\% TiO\textsubscript{2}. The observed variation in the \(E_{\text{optical}}\) values confirms that there is a change in the relative concentration of non-bridging oxygen atoms in the glass with incorporation of TiO\textsubscript{2}. For glass containing 2.5 mole\% TiO\textsubscript{2} the relative concentration of non-bridging oxygen atom is higher compared to the ‘base glass’ glass. The negative charge present in the non-bridging oxygen atoms facilitates the excitation of electrons to higher energy levels thereby decreasing the \(E_{\text{optical}}\) value. For 5 mole\% containing glasses, the decrease of \(E_{\text{optical}}\) value indicated that some more non-bridging sites have been created due to incorporation of more TiO\textsubscript{2}. However, the glasses containing more than 5 mole\% TiO\textsubscript{2}, no additional non bridging oxygen formation taking place as revealed from the comparable \(E_{\text{optical}}\) values for all three glasses (Ti-5, Ti-7.5 and Ti-10). From these results it
can be inferred that at higher concentration of TiO$_2$, Ti$^{4+}$ mainly goes to the network rather than further modifying the network and increasing the concentration of non bridging oxygen atoms. In other words, Ti$^{4+}$ acts as network modifier/former depending upon the concentration in glass. This fact was also confirmed from the FTIR and $^{11}$B MAS NMR results described above.

Figure 4-14: Tauc plots for Cs borosilicate glasses containing different amounts of TiO$_2$.

4.9 Discussion on Cs leaching and volatilization from structural aspect

The variation in the Cs volatilization and leaching behavior as a function of composition of the glass can now be explained with the help of structural information obtained
from the results of FTIR, $^{11}$B MAS NMR and uv-visible optical absorption studies. In base sodium borosilicate glasses containing Cs (‘base glass’), both Na$^+$ and Cs$^+$ ions occupy the network modifying sites, viz., (Si-O$^-$) and BO$_4^-$.

When part of B$_2$O$_3$ is substituted with TiO$_2$, initially (up to 2.5 mole% TiO$_2$), the relative concentration of BO$_4$ structural units increases as revealed by the $^{11}$B MAS NMR studies. As a results of this, some of the alkali metal ions get attached to the non bridging oxygen atoms of Si or Ti, instead of BO$_4^-$ structural units, which was also supported by FTIR studies (increase in number of non-bridging oxygen atoms) described above. The location of Cs/Na ions shift from the vicinity of BO$_4^-$ structural units to that of Si/Ti structural units can be one of the possible reasons for the decrease of leach rate of alkali ions in the glass. It is also possible that there can be some preferential interaction of Cs and Na ions with the Si/Ti structural units and that may be the possible reason for the difference in leaching characteristics of Na and Cs ions from the glass. However in this study we do not have any evidence for such preferential interaction of Na and Cs ions with the glass structural units. Nevertheless, FTIR, $^{11}$B MAS NMR and UV visible absorption studies revealed that the number of non bridging oxygen remained more or less constant after addition of 5 mole% TiO$_2$ or more. This confirmed that the excess TiO$_2$ is accommodated in glass network in forming silicotitanate type of cavity structural units where Cs$^+$ ions fit tightly, thus lowering lattice energy and in turn leading to lower leaching rate of Cs$^+$ ion.

The Cs volatilization behavior can also be explained to a certain extent by the structural information obtained from FTIR, $^{11}$B MAS NMR and uv-visible optical absorption studies described above. Cs volatilization mostly occurs during the melting stage, as confirmed from Fig.4–4. It is assumed that the structural configurations existing at the melting stage remains the same of the glassy state as the structural configurations get trapped during the quenching of the
melt. With the presence of Ti$^{4+}$, either at the network modifying or network forming sites, the interactions between the Ti$^{4+}$ and Cs$^+$ ions exists and this can result in the lower Cs volatilization loss when compared to the glass without any TiO$_2$. However, the observed variation in Cs-volatilization loss for higher TiO$_2$ concentration could not be understood.

4.10 **Summary of the results and conclusions**

Results of present study on physico-chemical properties of Cs borosilicate glasses containing TiO$_2$ are summarized as follows.

1. The glasses prepared with incorporation of TiO$_2$ at the expense of B$_2$O$_3$ showed decrease in the extent of Cs volatilization.

2. The increase of TiO$_2$ content in glass resulted in improvement in chemical durability. This is attributed a combined effect of TiO$_2$ increase and B$_2$O$_3$ content decrease.

3. Based on the structural information obtained through FTIR, $^{11}$B MAS NMR and uv-visible optical absorption studies, it is inferred that TiO$_2$ at lower concentration acts as a network modifier, while incorporation of more TiO$_2$ it goes to glass as network former.

4. Presence of TiO$_2$ as network former affects the bonding nature of Na-O and Cs-O linkages in the glass.

5. From our studies, it can be concluded that 5 mole% TiO$_2$ incorporation in the glass gives the most suitable glass composition, possessing reasonably low leach rate and minimum Cs volatilization losses.