Chapter 3

Studies on Sodium Aluminium Titano-Phosphate Glasses

3.1 Introduction

Phosphate glasses are finding ever-increasing applications in different emerging fields viz: vitrification of radioactive waste [103-105], photonics [39], fast ion conductor [106], glass-to-metal seals [107], biomaterials etc [108-109]. These glasses have a series of interesting properties such as low $T_g$, lower $T_m$ (compared to silicate glass), high TEC, high ultraviolet transmission and biocompatibility [38] which make them potential candidates for various technological applications. Earlier, phosphate glasses have been of limited interest due to their hygroscopic nature and poor chemical durability however, the development of novel compositions of superior physical and chemical properties, of these glasses have revived new interest in phosphate glasses and glass-ceramics. In recent years there has been much research on improving the physical properties and chemical durability of phosphate glasses by introducing intermediate type metal oxides (MO) like $\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3$, $\text{TiO}_2$, $\text{ZnO}$, which generate additional O-M-O type cross-linkages among different polyphosphate anions.

Alkali alumino-phosphate glasses are technologically important for low temperature hermetic sealing and vitrification of radioactive waste. These glasses are also important as laser host materials. These glasses with high alkali concentration have potential applications in solid state ionic devices. Sodium alumino-phosphate (NAP) glasses have $T_g$ below 400°C and TEC greater than $150 \times 10^{-7}/°\text{C}$ and are used for making glass-to-metal seals with low melting and high thermal expansion materials like Al, Cu etc. The NAP glasses have been the subject of various investigations [110-115]. The role of $\text{Al}_2\text{O}_3$, on structure and other
properties of these phosphate glasses, has been extensively studied [111-113]. It has been reported that addition of Al\textsubscript{2}O\textsubscript{3} up to ~10 mol\% to the phosphate glasses resulted in improved chemical durability and modifications in their thermo-physical properties like TEC and T\textsubscript{g}. These properties have shown marginal changes upon addition of more than 10 mol\% Al\textsubscript{2}O\textsubscript{3} [110]. Similarly, sodium titano-phosphate (NTP) glasses without Al\textsubscript{2}O\textsubscript{3} have also been investigated by many researchers [116-119]. Incorporation of TiO\textsubscript{2} improves the chemical durability of the phosphate glasses, while also increasing the nonlinear refractive index (n\textsubscript{2} values) [120], thereby facilitating their application as active materials in optical switches and telecommunication fibers. Presence of Al\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2} together in the glass matrix is expected to significantly modify the optical and thermo-physical properties of the glassy system. Therefore, effect of TiO\textsubscript{2} in NAP glasses in terms of thermo-physical and optical properties has been investigated in the present work and correlated with the structural changes in the glass.

3.2 Experimental

3.2.1 Synthesis of glass samples

Sodium aluminium titano-phosphate (NATP) glasses having compositions (in mol\%): 40Na\textsubscript{2}O-10Al\textsubscript{2}O\textsubscript{3}-xTiO\textsubscript{2}-(50-x)P\textsubscript{2}O\textsubscript{5}, where x = 0-20 were prepared by melt quench method. Analytical grade NaNO\textsubscript{3}, Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2} and NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4}, were used as starting materials in such proportions that the O/P ratio changed from 3.2 to 4.33. Glasses were prepared following the procedure as described in chapter 2 of the thesis. Depending on the composition, glass charges were melted in temperature range from 1250°C to 1350°C in the air ambient.
Annealing of these glasses was done in the temperature range ~400-460°C for 4 h. Annealed glasses were stored in a desiccator for further characterization.

### 3.2.2 Thermo-physical characterization

Density of glass samples was measured at room temperature by Archimedes principle using toluene as an immersion liquid with an accuracy of ± 0.03 g/cm³. Molar volume of the glass was also obtained from the density. TEC and $T_g$ were measured by TMA. The TEC being reported here are an average in the range of ~30-300°C. The MH of optically polished glass samples was measured by the Vickers indentation technique.

The effect of ambient moisture on the NATP glasses was also investigated. For this purpose, optically polished transparent glass discs of all compositions were exposed to air ambient and surface of glasses was examined by an optical microscope after different time intervals.

### 3.2.3 Optical characterization

Optical absorption and luminescence measurements of glass samples at room temperature were carried out as described in chapter 2. Polished glass samples having diameter more than 12 mm and thickness in the range 2-4 mm were used for these measurements. The samples were excited at 273 nm.

### 3.2.4 Structural characterization

Information regarding the structural aspect of the glass is essential to explain and understand the observed variation in the physical properties of the system as a function of the
composition. Therefore, structural aspects of these glasses have been investigated through $^{31}\text{P}$ and $^{27}\text{Al}$ MAS-NMR, Raman and FTIR techniques.

Raman spectra on polished glass discs were recorded as described in chapter 2. FTIR spectra of all glasses were recorded over the frequency range 400-4000 cm$^{-1}$ with a resolution of $\sim 4$ cm$^{-1}$ as detailed in chapter 2.

$^{31}\text{P}$ and $^{27}\text{Al}$ MAS-NMR spectra were recorded with the Bruker Avance 500WB spectrometer with a static field of 11.7 T. The spinning frequency of 15 kHz and 10 kHz were used for recording $^{31}\text{P}$ and $^{27}\text{Al}$ spectra, respectively. $^{31}\text{P}$ spectra were recorded at Larmor frequency 202.4 MHz and chemical shift values are expressed with respect to 85 % H$_3$PO$_4$. Typical 90° pulse duration and delay times are 3.5 $\mu$s and 4s, respectively. A number of NMR experiments had been carried out with different delay times and found that the 4s delay time for these samples was optimal. $^{27}\text{Al}$ spectra were recorded at Larmor frequency of 130.287 MHz with 2.5 $\mu$s pulses and 2s recycling time and chemical shift values are expressed relative to 1M aqueous solution of AlCl$_3$. The $^{31}\text{P}$ MAS-NMR spectra were deconvoluted based on Gaussian fit, by independently varying the peak maximum, line width and intensity. The quality or the goodness of the fit was judged from the $\chi^2$ values and the fit with lowest $\chi^2$ value was used to calculate the relative concentration of different P structural units.

3.3 Results and Discussion

3.3.1 XRD

Clear, transparent and bubble-free glasses were obtained for all the investigated compositions. Nominal batch compositions and O/P ratio of all NATP glasses are given in
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Table 3.1. Powder X-ray diffraction patterns for all the glass samples showed a broad hump at around $2\theta = 30^\circ$ as shown in Figure 3.1, characteristic of the amorphous nature of the glass samples.

Table 3.1: Nominal composition and O/P ratio for NATP glasses.

<table>
<thead>
<tr>
<th>Glass ID</th>
<th>Composition (Nominal) (mol%)</th>
<th>O/P ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na$_2$O Al$_2$O$_3$ P$_2$O$_5$ (x) TiO$_2$</td>
<td></td>
</tr>
<tr>
<td>NATP0</td>
<td>40 10 50 0</td>
<td>3.2</td>
</tr>
<tr>
<td>NATP2</td>
<td>40 10 48 2</td>
<td>3.27</td>
</tr>
<tr>
<td>NATP5</td>
<td>40 10 45 5</td>
<td>3.39</td>
</tr>
<tr>
<td>NATP10</td>
<td>40 10 40 10</td>
<td>3.63</td>
</tr>
<tr>
<td>NATP15</td>
<td>40 10 35 15</td>
<td>3.93</td>
</tr>
<tr>
<td>NATP20</td>
<td>40 10 30 20</td>
<td>4.33</td>
</tr>
</tbody>
</table>

Figure 3.1: XRD patterns of NATP glasses having x mol% TiO$_2$ (x = 0-20).
3.3.2 Thermo-physical properties

Various thermo-physical properties like $T_g$, TEC, MH, $\rho$ and $V_m$ for the prepared glass samples are given in Table 3.2.

Table 3.2: TiO$_2$ content (x), $T_g$, TEC, MH, $\rho$, $V_m$ and $E_{\text{optical}}$ for different NATP glasses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TiO$_2$ content x (mol%)</th>
<th>$E_{\text{optical}}$ (eV)</th>
<th>$T_g \pm 2$ ($^\circ$C)</th>
<th>TEC $\pm$ 5% ($10^{-7}/^\circ$C)</th>
<th>MH $\pm$ 5% (GPa)</th>
<th>$\rho \pm 0.03$ ($10^3$ kg/m$^3$)</th>
<th>$V_m$ ($10^{-4}$ m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NATP0</td>
<td>x = 0</td>
<td>3.57</td>
<td>386</td>
<td>186.40</td>
<td>2.90</td>
<td>2.63</td>
<td>40.29</td>
</tr>
<tr>
<td>NATP2</td>
<td>x = 2</td>
<td>3.43</td>
<td>415</td>
<td>168.50</td>
<td>3.05</td>
<td>2.66</td>
<td>39.37</td>
</tr>
<tr>
<td>NATP5</td>
<td>x = 5</td>
<td>3.34</td>
<td>448</td>
<td>158.06</td>
<td>3.25</td>
<td>2.68</td>
<td>38.38</td>
</tr>
<tr>
<td>NATP10</td>
<td>x = 10</td>
<td>3.32</td>
<td>479</td>
<td>157.50</td>
<td>3.35</td>
<td>2.72</td>
<td>36.67</td>
</tr>
<tr>
<td>NATP15</td>
<td>x = 15</td>
<td>3.30</td>
<td>472</td>
<td>168.27</td>
<td>3.31</td>
<td>2.70</td>
<td>35.80</td>
</tr>
<tr>
<td>NATP20</td>
<td>x = 20</td>
<td>3.29</td>
<td>462</td>
<td>165.25</td>
<td>3.23</td>
<td>2.46</td>
<td>37.03</td>
</tr>
</tbody>
</table>

Variations in $\rho$ and $V_m$ of the NATP glasses as a function of TiO$_2$ content (x) are shown in Figure 3.2. The $\rho$ first increases up to 10 mol%, and then decreases with further addition of the TiO$_2$. However, the $V_m$ first decreases and then increases. The observed variation, particularly below 10 mol% TiO$_2$ contents, is in contrary to one’s expectation as the molecular weight of P$_2$O$_5$ and TiO$_2$ are 142 g/mol and 79.9 g/mol, respectively and replacement of P$_2$O$_5$ by TiO$_2$ is expected to decrease the $\rho$ and increase the $V_m$. Observed variation in the above properties indicates that the Ti polyhedra form some new interconnections within the network and thus densify the glass network up to 10 mol% TiO$_2$. For glass samples with TiO$_2$ more than 10 mol% the $\rho$ decreases and $V_m$ increases. This indicates that for more than 10 mol% TiO$_2$ content, interconnections provided by titanium
polyhedra are not sufficient to overcome the depolymerization of phosphate network and result in decrease in $\rho$ and increase in the $V_m$.

**Figure 3.2:** Variation of density and molar volume of NATP glasses as a function of TiO$_2$ concentration ($x$) in mol%. Solid lines are drawn as guide to the eyes.

**Figure 3.3:** Variation of MH, TEC and $T_g$ of NATP glasses as a function of TiO$_2$ concentration ($x$) in mol %. Solid lines are drawn as guide to the eyes.
Variation in the values of MH, TEC and $T_g$ of the NATP glasses as a function of TiO$_2$ content are shown in Figure 3.3. It is clear from the figure that the $T_g$ and MH increase while TEC decreases up to 10 mol% TiO$_2$. With the increase of TiO$_2$, beyond 10 mol%, the $T_g$ and MH decrease and TEC increases. The initial increase in $T_g$ and MH values for replacement of TiO$_2$ by P$_2$O$_5$ up to 10 mol% indicates the formation of strong and rigid bonding. However, beyond that the network bonding weakens. The results of TEC measurement also support the observation that glass structure becomes more stable and rigid up to 10 mol% TiO$_2$ and beyond that network stabilization and rigidity start to reduce.

### 3.3.3 Optical properties

UV-Vis optical absorption spectra of the NATP glass samples containing different amounts of TiO$_2$ are shown in Figure 3.4. All the absorption curves are characterized by a broad onset of absorption edge over the region of 500-300 nm, which is characteristic of the glassy nature of the sample. The broad onset is arising due to the disorder in structural units existing in the glass. There is a distribution in the bond angles and bond lengths corresponding to different structural units in the glass and this is associated with the relaxation of selection rules for various optical transitions [121-122]. Such relaxation in the selection rules leads to broadening of the onset corresponding to the absorption edge. For the glass sample without any TiO$_2$ the onset of absorption is found to be around 350 nm. With incorporation of TiO$_2$, the onset of absorption was found to be red shifted for all the samples. Further, there is a weak absorption over the region of 400-500 nm in all the spectra. A similar weak absorption has also been observed in many phosphate and silicate based glasses [123-124]. Based on those reports we attribute this to the absorption due to the localized centers/structural
inhomogeneities present in the glass. (Presence of Ti$^{3+}$ in glass is characterized by an absorption in the visible region around 500-600 nm. However, formation of Ti$^{3+}$ species is unlikely in the glass samples of present study as the glass samples are prepared by melting the constituents in air at 1350°C).

Figure 3.4: UV-visible optical absorption spectra of NATP glasses containing different amounts of TiO$_2$ (x) in mol%.

Figure 3.5: Tauc plots for NATP glasses containing different amounts of TiO$_2$ (x) in mol%.
As the onsets of absorptions are quite broad, attempt was not made to exactly calculate the onset wavelength of absorption. However, the absorption coefficient ($\alpha$) in these glasses can be related to $E_{\text{optical}}$ values of the glass by a power law suggested by Mott and Davis [125], which can be expressed as $\alpha h\nu = A(E-h\nu)^{r}$, where $A$ is a constant and $r$ is a parameter which depends on the type of transitions and can have values 2, 3, $\frac{1}{2}$ etc. As reported by Tauc [121] and, Mott and Davis [125] for indirect transitions in glassy materials, the value of $r$ can be assumed to be 2. Hence, a plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ (known as a Tauc plot), will results in a curve, extrapolation of the linear region of the curve to the x-axis with $\alpha = 0$ can give the value of the optical gap in the glass. Tauc plots (variation of $(\alpha h\nu)^{1/2}$ as a function of $h\nu$) of NATP glasses are shown in Figure 3.5. The $E_{\text{optical}}$ values obtained from these Tauc plots are summarized in Table 3.2. For glass sample without any TiO$_2$ content, the $E_{\text{optical}}$ value is found to be 3.57 eV. Incorporation of 2 mol% TiO$_2$ resulted in reduced $E_{\text{optical}}$ value to 3.43 eV. Further, reduction in $E_{\text{optical}}$ value (3.34 eV) was noted for the glass containing 5.0 mol% TiO$_2$. The $E_{\text{optical}}$ values for the glasses containing 10, 15 and 20 mol% TiO$_2$, as mentioned in the Table 3.2, are comparable with that of the glass sample with 5 mol% TiO$_2$. The observed variation in the $E_{\text{optical}}$ values can be explained based on the conversion of BO to NBO atoms brought about by the TiO$_2$ incorporation in the glass. Optical transitions from these glasses are thought to be arising from the excitation of electrons from the levels, mainly constituted by oxygen atoms to the levels made by the metal ions. The negative charge present on the NBO atoms facilitates the excitation of its electrons to a higher energy level compared to BO atoms where there is no negative charge. Hence an increase in the concentration of NBO atoms is associated with a decrease in the $E_{\text{optical}}$ values. Similar a decrease in the $E_{\text{optical}}$ values with increase in NBO atoms content has been reported in many phosphate and silicate glasses [126-127]. In the present study, for glasses containing...
2 and 5 mol% TiO$_2$ the relative concentration of NBO atoms are higher and hence their $E_{optical}$ values are lower, when compared to the glass without any TiO$_2$. However, for the glass samples containing more than 5 mol% TiO$_2$, there is no significant change in the $E_{optical}$ values indicating that the relative concentration of NBO atoms attached with P structural units remains more or less same. 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 NBO atoms. There are no charge transfer phenomena taking place in these glasses, as this will lead to the reduction of Ti$^{4+}$ to Ti$^{3+}$ species, which is unlikely for glass samples prepared at 1350°C in air. Indeed, it is worth mentioning here, that the Ti$^{3+}$ species are mainly observed in glass samples prepared under reducing conditions [128-131].

![Emission spectrum of NATP glasses](image)

Figure 3.6: Emission spectrum of NATP glasses with (a) $x = 0$, (b) $x = 10$ and (c) $x = 20$ TiO$_2$ content (in mol%). The samples were excited at 273 nm.
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Emission spectra of a few representative NATP glass samples are shown in Figure 3.6. For the glass sample without any TiO$_2$, a broad peak centered about 435 nm with significant tailing towards higher wavelength region occurs (Figure 3.6(a)). The broad emission spectrum has been attributed to the different types of luminescent centres present in the glass. It is reported that in binary silicate [123] and phosphate glasses [132-133] linkages like Si-O…Na$^+$, P-O…Na$^+$ etc form and these linkages act as localized levels in the optical gap of the glasses and can trap the electrons. Such levels are generally known as L-centres or modified L-centres [123,132-133]. Recombination of electrons form this level with the holes in the lower levels leads to light emission. In a multi-component glass there can be a variety of L-centres and depending upon their concentration in the glass a broad emission spectrum is observed. With incorporation of TiO$_2$ at the expense of P$_2$O$_5$, upto 10 mol%, the wavelength corresponding to the emission maximum remained the same, even though there is a slight change in the line shape (Figure 3.6(b)). However, above 10 mol% TiO$_2$ incorporation in the glass, the emission maximum got significantly shifted to higher wavelength (528 nm) indicating a decrease in the energy corresponding to localized levels. From the UV-visible optical absorption spectrum it is confirmed that the $E_{\text{optical}}$ value decreases with increase in TiO$_2$ content in the glass. In accordance with this the emission maxima also get red shifted. Based on UV-Visible optical absorption and luminescence studies described above, it is inferred that, the glass network and the electronic environment around the NBOs change significantly with TiO$_2$ incorporation in the glass. The changes are with respect to the creation of more NBO atoms and formation of relatively more ionic P-O-Ti linkages at the expense of more covalent P-O-P linkages. Similar changes in the L-centre emission characteristics have also been observed in PbO-Na$_2$O-SiO$_2$ glasses [123]. At this stage it is
worthwhile to mention that no Ti$^{3+}$ emission is observed from the sample as reported by Bausa et al [129] and Batyaev et al [131].

### 3.3.4 Structural studies

In order to understand the observed variation in thermo-physical properties and $E_{\text{optical}}$ values, structural studies were carried out using $^{31}$P and $^{27}$Al MAS-NMR, Raman and FTIR techniques.

#### 3.3.4.1 MAS-NMR

$^{31}$P MAS-NMR spectra for NATP glasses, prepared with different amounts of TiO$_2$, are shown in Figure 3.7.

![Figure 3.7: $^{31}$P MAS-NMR spectra of NATP glasses having x mol% TiO$_2$ (x = 0-20). Side bands are marked with an asterisk (*).]
For the glass with $x = 0$, an asymmetric peak around -18 ppm with shoulders around -4 and +4 ppm has been observed. Deconvolution based on a Gaussian fit, revealed three peaks around -18.8, -4 and +4 ppm, which are characteristic of $Q^2$, $Q^1$ and $Q^0$ structural units of ‘P’, respectively (where $Q^n$ represents the ‘P’ structural units having ‘n’ number of bridging oxygen atoms) [134-135]. With the increase of TiO$_2$ concentration in the glass up to 10 mol%, the concentration of $Q^1$ structural units increases at the expense of $Q^2$ structural units as shown in the Figure 3.8(a). Furthermore, the $Q^2$ structural units show systematic increase in the chemical shift values from –18.8 ppm (for $x = 0$ mol%) to –11 ppm (for $x = 10$ mol%), while that of $Q^1$ structural units remain more or less the same, as shown in Figure 3.8(b). Beyond 10 mol% TiO$_2$, featureless $^{31}$P MAS-NMR spectra were observed with peak maxima shifting towards more positive values.

![Figure 3.8](image)

**Figure 3.8:** (a) Relative contents and (b) chemical shift values of $Q^1$ and $Q^2$ structural units as a function of TiO$_2$ content ($x$) in mol% in the glasses. Solid lines are drawn as guide to the eyes.

Increase in the concentration of $Q^1$ structural units in the glass is due to the depolymerization of polyphosphate chains as TiO$_2$ replaces the P$_2$O$_5$ in the glass (thus O/P ratio of the glass also increases). The increase in chemical shift of $Q^2$ structural units has been
attributed to a combined effect of decrease in chain length as well as the formation of P-O\(^{-}\)Ti\(^{4+}\) linkages (where Ti\(^{4+}\) exists at the network modifying positions in the glass) at the expense of P-O-P linkages [117]. Due to lower Z/r values of Ti\(^{4+}\) compared to P\(^{5+}\)(where Z is the valency of the ion and r is the ionic radius), replacement of the P-O-P linkages with P-O\(^{-}\)Ti\(^{4+}\) linkages results in an increase in \(^{31}\)P chemical shift values. For TiO\(_2\) content >10 mol\%, only one peak was observed with peak maxima shifting towards more positive values with increase in TiO\(_2\). Based on the chemical shift values and O/P ratios of the glass samples (Table 3.1), it is inferred that glass NATP15 (O/P ratio = 3.93) consists mainly of Q\(^{0}\) structural units along with some Q\(^{1}\) structural units and glass NATP20 (O/P ratio = 4.33) contains only Q\(^{0}\) structural units connected to different cations. For the glass sample containing more than 5 mol\% TiO\(_2\), the observed changes in the \(^{31}\)P MAS-NMR spectra can be explained by the formation of covalent P-O-Ti linkages (where Ti\(^{4+}\) act as network former) at the expense of P-O-P linkages. This is because the P structural units like Q\(^{1}\) and Q\(^{0}\) can not form a network of its own at this stage. In other words, TiO\(_2\) acts as a network former in these glasses when their concentration is above 10 mol\%. Similar network former and modifying behaviour of TiO\(_2\) has also been observed in borosilicate glasses containing different amounts of TiO\(_2\)[126].

\(^{27}\)Al MAS-NMR spectra of NATP glasses are shown in Figure 3.9. The spectra clearly show a change in the coordination environment around Al\(^{3+}\) ions in the glass as TiO\(_2\) substitutes the P\(_2\)O\(_5\). The NMR spectrum of NAP (x=0) glass shows a single peak around -20 ppm, characteristic of AlO\(_6\) structural units [136]. With increasing x, two additional peaks around +6 and +40 ppm start appearing. These peaks have been assigned to the five fold AlO\(_5\) and four fold AlO\(_4\) coordination of Al\(^{3+}\) ions respectively based on \(^{27}\)Al MAS-NMR
studies on alumino-phosphate crystals [136]. Intensity of these peaks increases progressively beyond x=10 mol%. For x=20, most of the Al\(^{3+}\) ions exist as AlO\(_4\) structural units. Based on \(^{27}\)Al MAS-NMR studies it is inferred that Al\(^{3+}\) ions mainly extend the glass network by forming P-O-Al type of linkages, where the Al\(^{3+}\) is having a tetrahedral configuration.

![Figure 3.9: \(^{27}\)Al MAS-NMR spectra of NATP glasses.](image)

3.3.4.2 Raman spectroscopy

The Raman spectra of NATP glasses in three frequency ranges, namely, low frequency (200-400 cm\(^{-1}\)), medium frequency (400-800 cm\(^{-1}\)) and high frequency (800-1400 cm\(^{-1}\)) ranges are shown separately in Figure 3.10. The low frequency Raman spectra are shown in Figure 3.10(a). A Raman band observed at ~300-400 cm\(^{-1}\) is typical of rocking motion of PO\(_4\) tetrahedron and/ or the motion of cationic polyhedrons [137]. The evolution of this peak ‘A’
(for NATP0), shows red shift towards the peak ‘B’ (for NATP20) with increasing TiO$_2$ content. Corresponding red shift is shown in the inset of Figure 3.10(a). Position of this band depends on the covalent interactions of metal cation with oxygen present in different coordination polyhedral units [137]. Therefore effect of TiO$_2$ on the extent of ionicity and/or covalency between the cations and its surrounding oxygen atoms is related to this low frequency Raman mode. We correlate the observed red shift in this peak to an increase in the ionicity with increasing TiO$_2$ content in accordance with the observation of Nelson and Exarhos [137]. This is quite understandable, as the covalency, which is related to the $Z/r$ ratio (where, $Z$ is the valency of the ion and $r$ is the ionic radius), decreases with increase in TiO$_2$.

A new peak ‘C’ at ~440 cm$^{-1}$, that starts developing for $x > 10$ mol% may be a characteristic of Na-O-P-O-Ti linkages. Similar structural units have been observed in compounds having NASICON type structure [138] exhibiting a Raman band at ~438 cm$^{-1}$.

The Raman spectra in the medium frequency range are shown in Figure 3.10(b). The band in the range ~650-750 cm$^{-1}$, associated the P-O-P symmetric stretching [139,140] is composed of two peaks namely ‘F’ and ‘G’ [Figure 3.10(b)]. This band in case of NATP0 has an intense peak ‘F’ at ~693 cm$^{-1}$, followed by a shoulder peak ‘G’ at ~737 cm$^{-1}$. Similar features are observed in the Raman spectra of NaPO$_3$ (sodium metaphosphate) as reported by Nelson and Tallant [140]. It has been reported that unlike in metaphosphates ($Q^2$ units), the pyrophosphates ($Q^1$ units) have only one peak centered at ~740 cm$^{-1}$ [140]. These results indicate that the peak ‘F’ is arising due to metaphosphate ($Q^2$) units and the shoulder ‘G’ is arising due to terminal PO$_3$ ($Q^1$) structural units. The decreasing intensity of peak ‘F’ and increasing intensity of peak ‘G’ with $x$, indicate that the terminal $Q^1$ structural units are evolving at the expense of the $Q^2$ structural units. These $Q^2$ structural units finally diminish...
beyond \( x = 10 \) mol\%. The width of this peak in the NATP20 glass (140 cm\(^{-1}\)) has been almost compared to that doubled of NATP0 (70 cm\(^{-1}\)). Yifen et al [141] have reported a Raman peak at 740 cm\(^{-1}\) for AlO\(_4\) structural units while Sakka et al [142] have assigned this Raman peak to Ti-O\(_{nb}\) (O\(_{nb}\): non-bridging oxygen) stretching vibrations in TiO\(_4\) units. Thus the random distribution of distorted TiO\(_4\) and AlO\(_4\) tetrahedra connected to different phosphate structural units may be responsible for the increase in the width of this peak. An additional peak ‘E’ at \( \sim 620 \) cm\(^{-1}\) (in NATP2) starts developing with addition of TiO\(_2\). The intensity of this peak increases with increasing TiO\(_2\). Based on previous studies, this peak is assigned to the stretching vibrations of Ti-O bonds in TiO\(_6\) units [139,142].

Figure 3.10(c) shows the Raman spectra in high frequency range 850-1300 cm\(^{-1}\) where, the different peaks are marked as ‘H’ through ‘L’. Inset of Figure 3.10(c) shows the shift in these peaks with TiO\(_2\) content. The NATP0 glass shows the most intense peak at \( \sim 1160 \) cm\(^{-1}\) (peak ‘K’) and a relatively less intense peak at \( \sim 1277 \) cm\(^{-1}\) (peak ‘L’). The line profile of the band (constituting peaks ‘K’ and ‘L’ in NATP0) is systematically altered as the concentration of TiO\(_2\) is increased. The symmetric and asymmetric stretching vibrations of Q\(^2\) structural units of ‘P’ (PO\(_2\) groups) appear at 1155 and 1280 cm\(^{-1}\), respectively [117,143].

Thus, the peaks ‘K’ and ‘L’ are assigned to the symmetric and asymmetric stretching vibrations of Q\(^2\) structural units of ‘P’. The peak ‘L’ is observed to show a red shift from 1273 cm\(^{-1}\) (for NATP0) to 1174 cm\(^{-1}\) (for NATP20). The peak ‘K’ appearing at 1163 cm\(^{-1}\) (for NATP0) also shows a red shift up to 1147 cm\(^{-1}\) (for NATP5), but to a lesser degree than peak ‘L’. At \( x = 10 \) mol\% and beyond, this peak disappears completely and is taken over by the shoulder peak ‘J’.
Figure 3.10: Raman spectra of NATP glasses having x mol% TiO$_2$ (a) Low frequency (200-400 cm$^{-1}$) Raman spectra; inset shows the shift of peak ‘A’ as a function of x (TiO$_2$ content), (b) Medium frequency (400-800 cm$^{-1}$) Raman spectra, (c) High frequency (800-1400 cm$^{-1}$) Raman spectra; inset shows the shift of various peaks as a function of x (TiO$_2$ content).

At a higher concentration of TiO$_2$, the shoulder at the left hand side of peak ‘K’ (in NATP2), develops into well defined peaks ‘I and J’. For the NATP5 glass, peaks ‘I and J’
appear at \( \sim 1010 \text{ cm}^{-1} \) and \( \sim 1090 \text{ cm}^{-1} \) respectively. For TiO\(_2\) above 10 mol\%, these peaks are further intensified, and the peak ‘K’ (quite intense at \( x = 0 \) mol\%) is completely diminished. The peaks (‘I’ and ‘J’) in NATP10 are red shifted to \( \sim 980 \) and 1060 cm\(^{-1}\). The line profiles in NATP15 and NATP20 have completely changed from that of NATP0. At \( x = 15 \) mol\%, the intensity of peak ‘I’ is more as compared to that of peak ‘J’ and therefore the combination peak (‘I’ and ‘J’) appears as a single asymmetric peak at \( \sim 1040 \text{ cm}^{-1} \). For NATP20 glass, there is a considerable overlap between peak ‘I’ and peak ‘J’ and appears as a single peak at 1015 cm\(^{-1}\). The Q\(^1\) units of pyrophosphate have Raman peaks in the range \( \sim 1050-1010 \text{ cm}^{-1} \) [139], similar to what we have observed in the form of peaks ‘I’ and ‘J’. The extinction of ‘K-L’ band together with the evolution of ‘I’ and ‘J’ peaks indicate that most of the Q\(^2\) structural units are being gradually converted into Q\(^1\) structural units. An additional peak ‘H’ at \( \sim 880 \text{ cm}^{-1} \) (in NATP2) is evolved with addition of TiO\(_2\). This peak for NATP5 and NATP10 is shifted to \( \sim 900 \text{ cm}^{-1} \) and finally to \( \sim 925 \text{ cm}^{-1} \) for NATP15 and NATP20. The intensity of this peak increases with increasing TiO\(_2\). Therefore, this peak is attributed to Ti-O\(_2\) stretching vibrations in TiO\(_4\) units [139,142].

This peak shows blue shift [inset of Figure 3.10(c)]. At lower content of TiO\(_2\), Ti-O-P linkages exist but as TiO\(_2\) content increases these Ti-O-P linkages are replaced by more of Ti-O-Ti linkages. In Ti-O-P linkages, the Ti-O bond strength is reduced compared to Ti-O bond strength in Ti-O-Ti linkages due to different charges of Ti and P (+4 and +5 respectively). As a result peak ‘H’ is shifted towards higher frequency, as more and more Ti-O-Ti linkages formed. The systematic red shift in ‘K’ and ‘L’ peaks, suggests redistribution of \( \pi \) bonding of terminal P=O bond, among various spectroscopically equivalent NBO’s as the Q\(^2\) units are systematically being converted into Q\(^1\) units [144]. In other words the ionicity of PO bonds increases with an increase in TiO\(_2\) content in the glasses.
3.3.4.3 FTIR spectroscopy

Room temperature infra-red spectra of all the NATP glass samples are shown in Figure 3.11. For the glass without TiO$_2$ ($x = 0$ mol%), five absorption bands approximately at 1280, 1200, 1120, 900, 750 cm$^{-1}$ are observed. Up to 10 mol% TiO$_2$, the IR patterns essentially remain the same except the intensity of bands around 1200 and 1280 cm$^{-1}$. The intensity of 1280 band keeps on diminishing and finally disappears at $x = 10$ mol%, while that around 1210 cm$^{-1}$ becomes pronounced. Above 10 mol% TiO$_2$, the IR spectra change significantly and the band at 900 cm$^{-1}$ disappears with the development of bands around approximate 1000, 1070 and 1170 cm$^{-1}$.

![Figure 3.11: FTIR spectra of NATP glasses.](image)

The band at 1280 cm$^{-1}$ has been attributed to the asymmetric stretching vibration of PO$_2$ groups (equivalent to $Q^2$ structural units) [145]. Both the absorptions bands around 1200
and 1120 cm\(^{-1}\) are assigned to asymmetric stretching of PO\(_3\) groups (chain end group equivalent to Q\(^1\) structural units). According to Montagne et al [146] the band around 1120 cm\(^{-1}\) is due to the vibration of PO\(_3\) groups with a smaller number of aluminium neighbours than those PO\(_3\) groups which are vibrating around 1200 cm\(^{-1}\). The band at 900 cm\(^{-1}\) is assigned to asymmetric stretching of P-O-P bridges [145-147]. The bands at 700 and 750 cm\(^{-1}\) are due to the symmetric stretching of P-O-P bridges [147-148]. A reduction in the intensity of the band at 1280 cm\(^{-1}\), while an increase in that around 1200 cm\(^{-1}\) indicate that as TiO\(_2\) content increases, the phosphate network depolymerize with the conversion of PO\(_2\) groups (Q\(^2\) structural units) into PO\(_3\) groups (Q\(^1\) structural units). This observation is in agreement with the NMR results that suggested a conversion of Q\(^2\) structural units to in Q\(^1\) structural units. Above 10 mol\% TiO\(_2\), the band at 900 cm\(^{-1}\) (corresponding to Q\(^1\) structural units) disappears with the development of bands approximately around 1000, 1070 and 1170 cm\(^{-1}\) characteristic of the isolated PO\(_4\) groups (equivalent to Q\(^0\) structural units) connected to different cations. These changes suggest that the phosphate network is highly depolymerized with isolated orthophosphates, which is in agreement with the NMR results.

MAS-NMR, Raman and FTIR spectroscopic studies revealed that the substitution of P\(_2\)O\(_5\) with TiO\(_2\) up to 10 mol\% depolymerizes the phosphate glass network by a systematic conversion of Q\(^2\) structural units into Q\(^1\). Even though Q\(^2\) to Q\(^1\) conversion occurs by breaking of P-O-P linkages, the formation of P-O-Ti (along with P-O-Al) bonds provide cross linking between ‘P’ structural units, which make the glass network more rigid. Therefore the net effect is an increase in T\(_g\), density and MH, and a decrease in molar volume and TEC, up to 10 mol\% TiO\(_2\). For the addition of TiO\(_2\) above 10 mol\%, the Q\(^1\) structural units get converted into Q\(^0\) units and TiO\(_4\) structural units leading to a Ti-O-Ti based network linked with discrete PO\(_4\) structural units. Further as the bond energy of Ti-O-Ti linkages is lesser
than P-O-P and P-O-Ti linkages, the formation of Ti-O-Ti type network connected with discrete ‘P’ structural units is expected to weaken the glass network. This is consistent with the decrease in $T_g$, density and MH, and an increase in molar volume and TEC for the glasses containing TiO$_2$ more than 10 mol%. The changes observed in the nature of the linkages present in the glass are also clear from the variation in the $E_{\text{optical}}$ values and wavelength corresponding to the emission maxima of the glass samples as a function of composition. When the strong P-O-P linkages are replaced by progressively weaker P-O-Ti or Ti-O-Ti linkages, the optical gap is expected to reduce. This will eventually lead to a decrease in the energy corresponding to the localized luminescence centres.

### 3.3.5 Surface degradation studies

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Figure 3.12: Initial optical photographs of NATP glass surfaces at 10x magnification.
Optical photograph of polished surfaces of all the NATP glasses are shown in Figure 3.12. We found no change in the surface of these glasses after exposure in air ambient for several months. However, after a long time exposure of the NATP0 glass (x = 0) resulted in the degradation of glass surface compared to other TiO$_2$ containing NATP glasses. Optical photograph of the same glass samples after an exposure to air ambient for 2 years are shown in Figure 3.13. These photographs clearly indicate a higher resistance of the NATP glasses having 5 mol% or higher amount of TiO$_2$ confirming the higher chemical durability of NATP glasses compared to NAP glass.

Figure 3.13: Optical photographs of different NATP glass surfaces, after an exposure to open air ambient for 2 years, at 10x magnification.
3.4 Conclusion

Raman, FTIR and $^{31}$P MAS-NMR studies confirm that the addition of TiO$_2$ in the NATP glass results in the progressive conversion of Q$^2$ structural units into Q$^1$ (up to 10 mol%) and Q$^0$ structural units (more than 10 mol%). The Raman spectra revealed that TiO$_2$ enters in the glass network in the form of octahedral and tetrahedral structural units and at a higher content of TiO$_2$ (for $x > 10$ mol%), existence of tetrahedral structural units of Ti are more favourable. Cross-linking provided by P-O-Ti and P-O-Al bonds between shortened discrete ‘P’ structural units (for $x \leq 10$ mol%) results into a more strong and rigid glass network.

Based on thermo-physical and structural studies it is concluded that TiO$_2$ behaves as a network modifier upto 10 mol% and above that a Ti-O-Ti based network connected with discrete PO$_4$ structural units exist in the glass. Al coordination changes significantly from octahedral to tetrahedral for glass samples having more that 10 mol% TiO$_2$. Above 10 mol% TiO$_2$ the incorporation depolymerization of glass network is significant with the formation of Ti-O-Ti type of linkages along with Q$^0$ structural units of P at the expense of strong P-O-P linkages leading to a less rigid structure. Variation in $T_g$, MH, density, TEC and $E_{optical}$ values for these glasses are in accordance with the structural changes taking place in the glass as a function of composition.