CHAPTER 5
STRUCTURE-PROPERTY CORRELATIONS IN Nb$_2$O$_5$-TeO$_2$ GLASSES

5.1 Introduction

In this chapter the results from various characterization techniques are discussed. Glasses from the system: xNb$_2$O$_5$-(100-x)TeO$_2$ glasses with x= 5, 10, 15 and 20 mol% are prepared and characterized by X-ray diffraction (XRD), density measurements, UV-visible absorption spectroscopy, differential scanning calorimetry (DSC) and Raman spectroscopy. Low-temperature specific heat measurements are performed on these glasses to study their low-temperature specific heat capacities and the phenomenon of boson peak.

5.2 Characterization Techniques

5.2.1 X-ray Diffraction (XRD)

XRD patterns of normal and splat quenched niobium tellurite glass samples are shown in Figs. 5.1 and 5.2, respectively.

![XRD patterns of normal-quenched niobium tellurite glasses.](image)

**Fig. 5.1** XRD patterns of normal-quenched niobium tellurite glasses.
The diffraction patterns of all glasses do not reveal any discrete or sharp peaks, but exhibit a broad halo at $2\theta = 26-29^\circ$, which reveals that all samples are amorphous.

### 5.2.2 Density

Density decreases from $5.533 \pm 0.003$ g cm$^{-3}$ to $5.229 \pm 0.002$ g cm$^{-3}$, in normally quenched glasses, and in splat-quenched glasses it decreases from $5.512 \pm 0.028$ g cm$^{-3}$ to $5.225 \pm 0.010$ g cm$^{-3}$ with the increase in Nb$_2$O$_5$ concentration from 5 to 20 mol %. Molar volume increases by large amount from 29.81 cm$^3$ mol$^{-1}$ to 34.59 cm$^3$ mol$^{-1}$ in normal quenched glasses when heavier Nb$_2$O$_5$ (Mol. Wt. = 265.82 amu) is substituted in place of lighter TeO$_2$ (Mol. Wt. = 159.60 amu) (Fig. 5.3 and Table 5.1). Similar trend in molar volume is observed in splat-quenched glasses.

The decrease in density is due to either the decrease in molecular weight of the glass sample or due to the increase in molar volume. Both molecular weight and molar volume increase with the increase in Nb$_2$O$_5$ concentration but the larger increase in glass molar volume (16%) is seen with increase in Nb$_2$O$_5$ concentration in comparison to smaller increase in molecular weight (10%). Therefore decrease in density is mostly due to expansion of glass volume. The trends in density agree with the values reported
by Blanchandin et al. where binary niobium tellurite glasses were prepared and their density values ranged from 5.45 to 5.22 g cm\(^{-3}\) with Nb\(_2\)O\(_5\) concentration varying from 5 to 20 mol\% [Blanchandin et al. (2002)]. Gaafar et al. prepared binary xNb\(_2\)O\(_5\)-(1-x)TeO\(_2\) glasses with x= 0.05, 0.1, 0.15, 0.20 and found similar values of density and molar volume [Gaafar et al. (2011)]. The decrease in our density values with increasing Nb\(_2\)O\(_5\) mol % is expected on the account of the additive density rule where the density of crystalline Nb\(_2\)O\(_5\) (4.600 g cm\(^{-3}\)) is lower than density of crystalline TeO\(_2\) (5.670 g cm\(^{-3}\)) [Lid (2000)]. The decrease in density is due to opening of tellurite network due to the conversion of TeO\(_4\) into TeO\(_3\) units and other structural modifications like the formation of Te-O-Nb bonds or voids. The increase in Nb\(_2\)O\(_5\) concentration generates free volume or produces voids in the glass network, the latter causes the reduction in density. Similar extraordinary large amounts of free volume were also reported in lead silicate glasses at high PbO concentrations [Kohara et al. (2010)].

Fig. 5.3 Density (d) and molar volume (V\(_{\text{M}}\)) of niobium tellurite glasses.
Molar volume is evaluated using the following relationship:

\[ V_M = \frac{\sum_i n_i M_i}{d} \]  \hspace{1cm} \text{(5.1)}

where

- \( n_i \) is molar fraction of the oxide component, \( i \)
- \( M_i \) is molecular weight of oxide component, \( i \)
- and \( d \) is the glass density.

Table 5.2 displays the density, molecular weight and molar volume data of crystalline oxide components.

Assuming the mixture of oxide components to be an ideal solution the additive oxide volume, \( V_o \) for each glass composition is calculated using the relation:

\[ V_o = \sum_i \frac{n_i M_i}{d_i} \]  \hspace{1cm} \text{(5.2)}

where,

- \( d_i \) is the density
- \( M_i \) is the molecular weight
- and \( n_i \) is the mol fraction of the \( i \)th component (crystalline oxide).

Excess volume, \( V_x \) is defined as the difference of \( V_M \) and \( V_o \).

\[ V_x = V_M - V_o \]  \hspace{1cm} \text{(5.3)}

where

- \( V_M \) is glass molar volume
- and \( V_o \) is additive crystalline oxide volume.

OPD is obtained using the following relationship:

\[ OPD = 1000 \times \frac{d \times (O)}{M} \]  \hspace{1cm} \text{(5.4)}

where

- \( d \) is the glass density
- \( (O) \) is the number of oxygen atoms per formula units
- and \( M \) is the molecular weight of glass [Altuf and Chaudhry(2010)].
Table 5.1 Density (d), molar volume ($V_M$), additive crystalline oxide volume ($V_o$), excess volume ($V_x$) and oxygen packing density (OPD) data of Nb$_2$O$_5$-TeO$_2$ glasses.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Nb$_2$O$_5$ mol %</th>
<th>d (g cm$^{-3}$)</th>
<th>$V_M$ (cm$^3$ mol$^{-1}$)</th>
<th>$V_o$ (cm$^3$ mol$^{-1}$)</th>
<th>$V_x$ (cm$^3$ mol$^{-1}$)</th>
<th>OPD (g atom liter$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5NbTe-n</td>
<td>5</td>
<td>5.533 ± 0.003</td>
<td>29.81</td>
<td>29.57</td>
<td>0.24</td>
<td>72.14</td>
</tr>
<tr>
<td>10NbTe-n</td>
<td>10</td>
<td>5.429 ± 0.003</td>
<td>31.36</td>
<td>30.98</td>
<td>0.38</td>
<td>73.36</td>
</tr>
<tr>
<td>15NbTe-n</td>
<td>15</td>
<td>5.329 ± 0.002</td>
<td>32.94</td>
<td>32.40</td>
<td>0.54</td>
<td>74.38</td>
</tr>
<tr>
<td>20NbTe-n</td>
<td>20</td>
<td>5.229 ± 0.002</td>
<td>34.59</td>
<td>33.81</td>
<td>0.78</td>
<td>75.18</td>
</tr>
<tr>
<td>5NbTe-s</td>
<td>5</td>
<td>5.512 ± 0.028</td>
<td>29.92</td>
<td>29.57</td>
<td>0.35</td>
<td>71.86</td>
</tr>
<tr>
<td>10NbTe-s</td>
<td>10</td>
<td>5.428 ± 0.012</td>
<td>31.36</td>
<td>30.98</td>
<td>0.38</td>
<td>73.34</td>
</tr>
<tr>
<td>15NbTe-s</td>
<td>15</td>
<td>5.324 ± 0.018</td>
<td>32.97</td>
<td>32.40</td>
<td>0.57</td>
<td>74.31</td>
</tr>
<tr>
<td>20NbTe-s</td>
<td>20</td>
<td>5.225 ± 0.010</td>
<td>34.61</td>
<td>33.81</td>
<td>0.80</td>
<td>75.12</td>
</tr>
</tbody>
</table>
Table 5.2 Density, molecular weight and molar volume data of crystalline oxide components.

<table>
<thead>
<tr>
<th>Oxide component</th>
<th>Molecular weight (amu)</th>
<th>Density (g cm(^{-3}))</th>
<th>Molar volume (cm(^3) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb(_2)O(_5) (Orthogonal)</td>
<td>265.82</td>
<td>4.47</td>
<td>59.47</td>
</tr>
<tr>
<td>TeO(_2) (Tetragonal)</td>
<td>159.60</td>
<td>5.67</td>
<td>28.15</td>
</tr>
</tbody>
</table>

The molar volume of niobium tellurite glasses is higher than molar volume of their starting crystalline oxides, which indicates that the addition of Nb\(_2\)O\(_5\) into glass network introduces excess structural volume (Table 5.1). The excess volume increases from 0.24 to 0.78 cm\(^3\) mol\(^{-1}\) in normal quenched glasses, and from 0.35 to 0.80 cm\(^3\) mol\(^{-1}\) in splat quenched glasses, with the increase in Nb\(_2\)O\(_5\) concentration from 5 to 20 mol\%. OPD increases from 72.14 g atom liter\(^{-1}\) to 75.18 g atom liter\(^{-1}\) in normal quenched glasses while in splat quenched glasses it is found to increase from 71.86 g atom liter\(^{-1}\) to 75.12 g atom liter\(^{-1}\) (Table 5.1). The above results are consistent with the results from DSC spectra (discussed later in section 5.2.4.). This increase in OPD is due to the fact that number of oxygen atoms contributed by each Nb\(_2\)O\(_5\) molecule is 2.5 and that is higher than that contributed by each TeO\(_2\) molecule (which is 2) and also Nb\(^{5+}\) ions, which exist as NbO\(_6\) octahedra connect Te-O chains and thereby increases the network connectivity.

5.2.3. UV-visible Absorption Spectroscopy

Both normal and splat quenched glasses are transparent and yellowish brown in colour. Figs. 5.4 and 5.5 display the UV-visible absorption spectra of normal and splat quenched niobium tellurite glasses, respectively. The optical absorption cut-off wavelength, \(\lambda_o\), is arbitrarily defined as the wavelength at which the absorption coefficient, \(\alpha\), increases abruptly. The optical absorption spectra shift towards longer wavelength region with the increase in Nb\(_2\)O\(_5\) concentration.
Fig. 5.4 UV-visible absorption spectra of normal-quenched niobium tellurite glasses.

Fig. 5.5 UV-visible absorption spectra of splat-quenched niobium tellurite glasses.
The optical cut off wavelength increases from 395 nm to 402 nm with increase in Nb₂O₅ concentration from 5 to 20-mol% (Fig. 5.6 and Table 5.3). Niobium tellurite glasses show an intense optical band just below the absorption cut-off in the wavelength range of 394-400 nm, which can be due to the electronic excitations of Nb⁵⁺ ions or even due to lone pair of electrons on Te atoms.

Table 5.3 Cut-off wavelength in normal and splat-quenched niobium tellurite glasses.

<table>
<thead>
<tr>
<th>Nb₂O₅ mol%</th>
<th>Cut-off wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>395</td>
</tr>
<tr>
<td>10</td>
<td>399</td>
</tr>
<tr>
<td>15</td>
<td>400</td>
</tr>
<tr>
<td>20</td>
<td>402</td>
</tr>
</tbody>
</table>

The equation for linear fit of the above graph is given below:

\[ \lambda_o = 393.5 + 0.44x \]  \hspace{1cm} \text{...(5.5)}

where \( x \) is Nb₂O₅ mol% and \( \lambda_o \) is cut-off wavelength.

![Fig. 5.6 Variation of \( \lambda_o \) with varying Nb₂O₅ mol% (denoted as x).]
5.2.4. Differential Scanning Calorimetry (DSC)

Glass transition, crystallization and melting peaks are determined from DSC spectra of samples and all glasses exhibit single glass transition. Glass transition temperature increases from 330°C to 416°C with increase in Nb$_2$O$_5$ concentration from 5-mol % to 20-mol % in normal-quenched niobium tellurite glasses, and it increases from 331°C to 420°C in splat-quenched glasses (Table 5.4).

Normally quenched glasses with lower Nb$_2$O$_5$ concentration show five exothermic crystallization peaks (sample code- 5NbTe-n), which reduces to a single crystallization peak at higher Nb$_2$O$_5$ concentrations (sample code- 20NbTe-n). Similar behaviour is observed in splat-quenched glasses (Figs. 5.7 and 5.8, Table 5.4). Glass transition temperature increases with the increase in Nb$_2$O$_5$ concentration which is due to higher bond strength of Nb-O bonds (bond enthalpy = 752.4 kJ/mol) than Te-O bond (bond enthalpy= 376 kJ/mol) [Sanghi et al. (2010); Mirgorodsky et al. (2012)]. The increase in Nb$_2$O$_5$ concentration strengthens the glass network by connecting the Te-O chains through NbO$_6$ octahedra as shown in Fig. 5.9 [Lin et al. (2009)]. DSC measurements on niobium tellurite glasses found that glass samples containing 5 mol % of Nb$_2$O$_5$ show five exothermic peaks at 396°C, 427°C, 476°C, 539°C and 555°C and a single endothermic peak at 692°C. The crystallization behaviour is significantly modified with the increase in Nb$_2$O$_5$ concentration. The multiple exothermic peaks observed in 5-mol% Nb$_2$O$_5$ glass disappear with the increase in Nb$_2$O$_5$ concentration to 20 mol%. The first exothermic peak at 396°C is due to the crystallization of δ-TeO$_2$ phase, the second peak at 427°C is due to the crystallization of γ-TeO$_2$ phase and to the transformation of δ-TeO$_2$ phase to α-TeO$_2$ phase, the third peak at 476°C is due to the crystallization of α-TeO$_2$ phase. The fourth peak at 539°C is due to the crystallization of Nb$_2$Te$_4$O$_{13}$ phase and the fifth peak at 555°C is due to the transformation of γ-TeO$_2$ to α-TeO$_2$ phase [Blanchandin et al. (1999)]. The absence of first two peaks at 396°C and 427°C for higher Nb$_2$O$_5$ ≥ 10 mol% indicates the absence of δ-TeO$_2$ and γ-TeO$_2$ phases.
Table 5.4 Glass transition ($T_g$), crystallization temperatures ($T_c$), melting temperatures ($T_m$), thermal stability range (S) and glass forming tendency (K) of niobium tellurite glasses (1, 2, 3, 4, 5 in subscripts represent multiple peaks and all the temperatures are in °C).

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Nb$_2$O$_5$ mol %</th>
<th>$T_g$</th>
<th>$T_{c1}$</th>
<th>$T_{c2}$</th>
<th>$T_{c3}$</th>
<th>$T_{c4}$</th>
<th>$T_{c5}$</th>
<th>$T_{m1}$</th>
<th>$T_{m2}$</th>
<th>S</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>5NbTe-n</td>
<td>5</td>
<td>330</td>
<td>396</td>
<td>427</td>
<td>476</td>
<td>539</td>
<td>555</td>
<td>693</td>
<td>-</td>
<td>97</td>
<td>0.37</td>
</tr>
<tr>
<td>10NbTe-n</td>
<td>10</td>
<td>357</td>
<td>500</td>
<td>529</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>693</td>
<td>740</td>
<td>143</td>
<td>0.74</td>
</tr>
<tr>
<td>15NbTe-n</td>
<td>15</td>
<td>387</td>
<td>522</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>691</td>
<td>771</td>
<td>135</td>
<td>0.80</td>
</tr>
<tr>
<td>20NbTe-n</td>
<td>20</td>
<td>416</td>
<td>541</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>736</td>
<td>125</td>
<td>0.64</td>
<td></td>
</tr>
<tr>
<td>5NbTe-s</td>
<td>5</td>
<td>331</td>
<td>425</td>
<td>477</td>
<td>536</td>
<td>552</td>
<td>-</td>
<td>694</td>
<td>-</td>
<td>94</td>
<td>0.35</td>
</tr>
<tr>
<td>10NbTe-s</td>
<td>10</td>
<td>358</td>
<td>504</td>
<td>531</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>694</td>
<td>741</td>
<td>146</td>
<td>0.77</td>
</tr>
<tr>
<td>15NbTe-s</td>
<td>15</td>
<td>388</td>
<td>512</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>691</td>
<td>771</td>
<td>124</td>
<td>0.69</td>
</tr>
<tr>
<td>20NbTe-s</td>
<td>20</td>
<td>420</td>
<td>542</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>736</td>
<td>760</td>
<td>122</td>
<td>0.63</td>
</tr>
</tbody>
</table>
The composition of niobium tellurite glasses is such that it produces Nb$_2$Te$_4$O$_{13}$ and TeO$_2$ phases on devitrification during DSC heating cycle by the following reaction:

\[ 5\text{Nb}_2\text{O}_5 - 95\text{TeO}_2 \rightarrow 5\text{Nb}_2\text{Te}_4\text{O}_{13} + 75\text{TeO}_2 \]  \( \text{(5.6)} \)

Similar equations can be written for glasses with higher Nb$_2$O$_5$ concentration.

Blanchandin et al. (1999) reported that the melting peak at 693°C is the eutectic point between crystalline Nb$_2$Te$_4$O$_{13}$ and TeO$_2$ phases as represented by the following equilibrium reaction:

\[ L_e \leftrightarrow \text{Nb}_2\text{Te}_4\text{O}_{13} + \text{TeO}_2 \]  \( \text{(5.7)} \)

The endothermic peak at 740-770°C corresponds to the incongruent melting of the Nb$_2$Te$_4$O$_{13}$ compound and to the equilibrium reaction [Blanchandin et al. (1999)]:

\[ \text{Nb}_2\text{Te}_4\text{O}_{13} \leftrightarrow L_p + \text{Nb}_2\text{Te}_5\text{O}_{11} \]  \( \text{(5.8)} \)

When the concentration of Nb$^{5+}$ ions is sufficiently high to connect Te-O chains, the glass network tends to homogenize and therefore only one crystalline compound, Nb$_2$Te$_4$O$_{13}$ is formed on devitrification [Lin et al. (2009)]. This is confirmed by the fact that niobium glasses with higher Nb$_2$O$_5$ mol % show only one exothermic crystallization peak at ~540°C which is due to the crystallization of Nb$_2$Te$_4$O$_{13}$ phase that subsequently melts at 760°C. The stoichiometry of glass with 20-mol % Nb$_2$O$_5$ (sample codes- 20NbTe-n and 20NbTe-s) is such that it produces only Nb$_2$Te$_4$O$_{13}$ crystalline phase without any precipitates of TeO$_2$ by the following reaction:

\[ 20\text{Nb}_2\text{O}_5 - 80\text{TeO}_2 \rightarrow 20\text{Nb}_2\text{Te}_4\text{O}_{13} \]  \( \text{(5.9)} \)

It should be mentioned here that according to new insights about the structure and properties of glasses from M$_x$O$_y$-TeO$_2$ system (where M= Nb and W ions) what gets formed during glass devitrification might not be actually Nb$_2$Te$_4$O$_{13}$ phase but crystalline solid solutions of TeO$_2$-M$_x$O$_y$ [Mirgorodsky et al. (2012)].

The normal and splat-quenched niobium tellurite glasses show similar thermal properties, but somewhat higher glass transition temperature is observed in splat quenched glasses. This is expected because splat-quenched glasses are frozen earlier, at a higher temperature.
Fig. 5.7 DSC spectra of normal-quenched niobium tellurite glasses.

Fig. 5.8 DSC spectra of splat-quenched niobium tellurite glasses.
The difference in glass transition temperature between normal and splat quenched glasses is maximum in glass with 20-mol % Nb$_2$O$_5$. The thermal properties of niobium-tellurite glass samples prepared in the present study are similar to those of glasses investigated by Blanchandin et al. [Blanchandin et al. (1999)]. However, Saddeek et al. did not report multiple crystallization peaks during DSC measurements on niobium tellurite glasses [Saddeek et al. (2008)]. This could be because the latter investigators used higher melting temperatures of 1025°C, which homogenized the initial melt, and hence the glass structure to a greater extent. This indicates that melt history plays an important role in influencing the tellurite glass structure and its crystallization properties.

The thermal stability range (S) for the glass is estimated using the following relationship:

$$S = T_c - T_g$$ ...

where $T_c$ is crystallization and $T_g$ is glass transition temperatures [El-Mallawany and Ahmed (2008)].

S provides a good estimate of the tendency of the glass to crystallize. The thermal stability of glasses increases from 97°C to 143°C with the increase in Nb$_2$O$_5$ from 5 to 10 mol%, and then it decreases to 125°C, with increase in Nb$_2$O$_5$ concentration from 10 to 20 mol%. These glasses are promising candidates for optical fibre drawing, since the later is a reheating process and any crystallization during the process will increase the scattering loss of the fiber and degrade the optical properties hence it is desirable for a glass host to have high thermal stability [Dai et al. (2005)]. Glasses containing 10 mol% of Nb$_2$O$_5$ (sample code- 10NbTe-n and 10NbTe-s) are most stable.

The glass-forming tendency (K), which is a useful measure of devitrification tendency for the glass, is given by:

$$K = \frac{T_c-T_g}{T_m-T_c}$$ ...

Where $T_g$, $T_c$, $T_m$ are glass transition, crystallization and melting temperatures, respectively [El-Mallawany and Ahmed (2008)].
Larger the K, stronger is the inhibition to nucleation and crystallization processes, and consequently, the more is the thermal stability of the glass. Low value of K indicates high tendency to devitrify. When Nb$_2$O$_5$ is introduced into the glass network, it provides oxygen ions to change some of TeO$_4$ tbps into TeO$_3$ bps, and further Nb$^{5+}$ ions, which exist as NbO$_6$ octahedra, connects the Te–O chains (Fig. 5.9).

![Systematic diagram of Nb$_2$O$_5$-TeO$_2$ glass network](Lin et al. (2009)).

At lower Nb$_2$O$_5$ concentration, there are insufficient linkages between Te–O chains due to insufficient amount of Nb$_2$O$_5$, which results in an inhomogeneous tellurite glass network. When Nb$_2$O$_5$ concentration is increased from 5 to 10 mol%, more and more Nb$^{5+}$ ions connect Te–O chains as NbO$_6$ octahedra, which tends to homogenize the glass network and strengthen the glass network, thereby increasing its thermal stability [Lin et al. (2009)]. The increase in Nb$_2$O$_5$ concentration leads to the conversion of TeO$_4$ to TeO$_3$ units and increases the distortion in the NbO$_6$ octahedra. The presence of more distorted NbO$_6$ octahedra and TeO$_3$ tp are responsible for the higher thermal stabilities of these glasses, since large thermal energy will be required to release the asymmetry and distortion [Murugan and Ohishi (2004)].
5.2.5. Low-Temperature Specific Heat Capacity Measurements

The specific heat capacity of niobium tellurite glasses is measured in the temperature range of 4-215 K, and the temperature dependence of $C_p/T^3$ is shown in Fig. 5.10. The low temperature data exhibits the usual glassy behaviour, with a broad maximum in $C_p/T^3$ between ~ 9 to 11K, which is known as the boson peak, is defined as low frequency vibrational modes, and are also observed in Raman and neutron scattering spectra [Buchenau et al. (1986); Gil et al. (1993)].

![Plot of $C_p/T^3$ vs. Temperature](image)

**Fig. 5.10** The plots of $C_p/T^3$ against temperature (T) for niobium tellurite glasses (Inset shows larger view of same graph).

A clear maxima, commonly known as the boson peak, is observed in all four niobium tellurite glasses, which reveals the existence of excess vibrational states above the expected Debye levels in glasses. It is found that with the increase in the concentration of Nb$_2$O$_5$ from 5 to 20 mol%, the maxima in $C_p/T^3$ decreases from 6.43 J mol$^{-1}$K$^{-4}$ to 5.48 J mol$^{-1}$K$^{-4}$. The addition of Nb$_2$O$_5$ to tellurite glass network shifts the temperature of maxima from 9.06 ± 0.01 to 10.88 ± 0.01 K with the increase in Nb$_2$O$_5$.
concentration from 5 to 20 mol%. The maxima in $C_p/T^3$ and the temperature of maxima are denoted by $P_c$ and $T_M$, respectively. The addition of $\text{Nb}_2\text{O}_5$ increases the internetworking of $\text{TeO}_4$ units and connects the Te-O chains through NbO$_6$ octahedral units. $T_M$ increases from 9.06 K to 10.09 K with the increase in $\text{Nb}_2\text{O}_5$ concentration from 5 to 10 mol%, but its maxima ($P_c$) decreases by 10% with increase in $\text{Nb}_2\text{O}_5$ concentration from 5 to 10 mol% (from 5NbTe-n to 10NbTe-n) and then $P_c$ undergoes only a slight decrease from 5.76 J mol$^{-1}$K$^{-4}$ to 5.48 J mol$^{-1}$K$^{-4}$ as $\text{Nb}_2\text{O}_5$ concentration is further increased from 10 to 20 mol% (Table 5.5). This indicates that boson peak not only represents the effect of $\text{Nb}_2\text{O}_5$ on tellurite glass network but also shows strong non-linearity that also evokes saturation effect at higher $\text{Nb}_2\text{O}_5$. The boson peak is related to the structural and elastic heterogeneity of glasses and is discussed by several authors [Schirmacher et al. (1998); Champagnon et al. (2009); Marruzzo et al. (2013)]. The decrease in the intensity of boson peak indicates the decrease in phonon scattering due to increase in the homogeneity of the glass structure, a result that agrees with the DSC findings, where multiple crystallization peaks are observed at low $\text{Nb}_2\text{O}_5$ concentration of 5 mol%, which reduce to single crystallization peak at higher $\text{Nb}_2\text{O}_5$ mol%. This is an indication of increase in homogeneity of glass structure with the addition of $\text{Nb}_2\text{O}_5$ mol%.

Liu and Löhneysen suggested that at intermediate temperatures, the specific heat of crystalline and glassy materials has a general correlation between the mechanisms related to the occurrence of maxima in $C_p/T^3$, namely $P_c$ and the temperature of maxima ($T_M$), i.e. $P_c \propto (T_M)^{-1.6}$ [Liu and Lohneysen (1996)]. Our low temperature data is plotted along with the earlier specific heat capacity data on crystalline and amorphous materials and it agrees very well with the proposed scaling of Liu and Löhneysen, showing that this scaling is useful towards the understanding of the low and intermediate temperature properties of solids (Fig. 5.11). The variation of $P_c$ with $(T_M)^{-1.6}$ in niobium tellurite glasses is shown in Fig. 5.12.
The low-temperature specific heat is given by the following relationship:

$$C_p = C_{\text{Debye}} \cdot T^3$$  \hspace{1cm} \ldots(5.12)

where

$$C_{\text{Debye}} = \frac{12}{5} \cdot \left(\frac{nR}{T_\theta}\right) = 234 \cdot \frac{nR}{T_\theta} \quad \text{at} \quad T \ll T_\theta$$ \hspace{1cm} \ldots(5.13)

$$\Rightarrow \quad C_p = 234 \cdot nR \left(\frac{T}{T_\theta}\right)^3$$ \hspace{1cm} \ldots(5.14)

where

n is total number of atoms,
R is gas constant
and $T_\theta$ is Debye’s temperature.

This is Debye’s $T^3$ law [Gopal (1966)].
Fig. 5.12 Variation of $P_c$ with $(T_M)^{1.6}$ in niobium tellurite glasses.

The slope of $C_p$ versus $T^3$ plots are used to evaluate Debye’s temperature ($T_\theta$). Debye temperature represents the temperature at which all modes of vibrations in a solid are excited [Halimah et al. (2010)] and it increases from 211K to 245K, this implies an increase in the rigidity of the glass with the increase in Nb$_2$O$_5$ concentration from 5 to 20 mol%, which is consistent with our findings from earlier studies. Table 5.5 gives the variation of maxima in $C_p/T^3$ ($P_c$), temperature of maxima ($T_M$) and Debye’s temperature ($T_\theta$) in niobium tellurite glasses. It is known from earlier studies and also from Raman study (discussed later in section 5.2.6) that NbO$_6$ octahedra increase with the increase in Nb$_2$O$_5$ concentration. NbO$_6$ octahedra and NBOs are responsible for the low-temperature anomalies in these glasses. The role of NBOs in network loosening works in competition with the role of NbO$_6$ octahedra in the stiffening of glass network, which results in the low-energy vibrations.
Table 5.5 Variation of maxima in $C_p/T^3$ ($P_c$), temperature of maxima ($T_M$) and Debye’s temperature ($T_\theta$) in niobium tellurite glasses.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>$P_c \times 10^{-4}$ (J mol$^{-1}$ K$^{-4}$)</th>
<th>$T_M$ (K)</th>
<th>$T_\theta$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5NbTe-n</td>
<td>6.43</td>
<td>9.06</td>
<td>211</td>
</tr>
<tr>
<td>10NbTe-n</td>
<td>5.76</td>
<td>10.09</td>
<td>233</td>
</tr>
<tr>
<td>15NbTe-n</td>
<td>5.67</td>
<td>10.58</td>
<td>237</td>
</tr>
<tr>
<td>20NbTe-n</td>
<td>5.48</td>
<td>10.88</td>
<td>245</td>
</tr>
</tbody>
</table>

The maxima in $C_p/T^3$, $P_c$ decreases from 6.43 to 5.48 J mol$^{-1}$ K$^{-4}$ and the temperature of maxima $T_M$ increases from 9.06 K to 10.88 K as glass transition temperature increases from 330°C to 416°C. Fig. 5.13 displays the variation of $P_c$ and $T_M$ with $T_g$.

![Fig. 5.13 Variation of $P_c$ and $T_M$ with $T_g$.](image-url)
Low-temperature specific heat capacity measurements on niobium tellurite glasses have been done for the first time. Earlier authors have reported the low-temperature specific-heat studies on Ag$_2$O-B$_2$O$_3$ glasses and found that the low-temperature excess specific heat increases with increasing silver oxide content. The source for this excess specific heat lies in low-energy vibrational states additional to the Debye contribution of the ordinary elastic waves, whose growing density is associated with the existence of oxygen ions in the borate network, which are non-bridging or bonded only to a single unit. NBOs causes a local breakdown of the structure, decreasing its coherence and giving rise to low-energy vibrations and the partial change of boron coordination from trigonal to tetrahedral [Tripodo et al. (1999)].

Halimah et al. studied \( \left\{ (\text{TeO}_2)_{70}(\text{B}_2\text{O}_3)_{30} \right\}_{100-z} [\text{Ag}_2\text{O}]_z \) glasses with \( z = 5, 8, 10, 13 \) and 15 mol\% and found that Debye temperature decreased with the increase in AgI which was due to progressively weakening of the glass structure due to the formation of NBOs that opens up the glass structure and thus the rigidity of glass network decreases [Halimah et al. (2010)].

5.2.6 Raman Spectroscopy

The intensity normalized Raman spectra of normal and splat-quenched niobium tellurite glasses are shown in Figs. 5.14 and 5.15, respectively. Raman spectra of both normal and splat quenched glasses are exactly same which indicates that same structural units are present and there is no difference in the glass short-range structure prepared at two quenching rates. Raman spectra are deconvoluted into 6 symmetric Gaussian peaks centred at approximately 455 cm$^{-1}$, 610 cm$^{-1}$, 660 cm$^{-1}$, 712 cm$^{-1}$, 769 cm$^{-1}$ and 876 cm$^{-1}$ using Peakfit software and two point baseline correction method [Khalil et al. (2010)]. The deconvoluted Raman spectra for glass sample containing 5 mol\% of Nb$_2$O$_5$ (sample code- 5NbTe-n) is shown in Fig. 5.16.

The peak at lower wave number, 455 cm$^{-1}$ is ascribed to the symmetric stretching and bending vibrations of Te-O-Te linkages, which are formed by sharing vertices of TeO$_4$ trigonal bipyramids (tbp’s), TeO$_{3+1}$ polyhedra and TeO$_3$ trigonal planar units [Kalampounias et al. (2006)]. The occurrence of this peak in our glass samples indicates the presence of continuous network consisting of Te-O polyhedra.
Fig. 5.14 The intensity-normalized Raman spectra of normal- quenched niobium tellurite glasses (The graphs are shifted for the sake of clarity).

Fig. 5.15 The intensity-normalized Raman spectra of splat- quenched niobium tellurite glasses (The graphs are shifted for the sake of clarity).
This band is due to networking of initially polymerized glass network, which slowly diminishes in intensity with the addition of Nb₂O₅, and is a signature of loss of connectivity due to the deformation of Te-O-Te linkages, which leads to the conversion of TeO₄ tpb units to TeO₃ tp units resulting in the formation of NBO atoms. Also breaking of Te-O-Te linkages leads to the decrease in Te-O coordination number, as explained by the earlier workers [Hoppe et al. (2004)].

Fig. 5.16 The deconvoluted Raman spectra of 5 mol% Nb₂O₅ glass (sample code-5NbTe-n).

Raman bands at ~610 cm⁻¹ and 660 cm⁻¹ are due to the Te-O bond stretching vibrations of TeO₄ units and similarly the bands at ~712 cm⁻¹ and 769 cm⁻¹ are due to the vibrations of Te-O bonds in TeO₃ units [Charton and Armand (2004)]. The two different frequencies are presumably related to the two non-equivalent oxygen atoms (those at the equatorial plane and those out of the plane). In gallate and silicate glasses containing niobium oxide, an additional band is observed around 650 cm⁻¹ (near band at 660 cm⁻¹ in present glasses) [Fukumi and Sakka (1989)]. This is attributed to the presence of less distorted NbO₆ octahedra without non-bridging oxygens. In the present niobium tellurite glasses, this band is overlapped with band at 610 cm⁻¹ as well as band at 660 cm⁻¹. The intensities of band at ~610 cm⁻¹ and 660 cm⁻¹ are found to decrease while the intensities of bands at ~712 cm⁻¹ and 769 cm⁻¹ increase with the increase in Nb₂O₅ concentration, which clearly indicates the increase in concentration of TeO₃ units.
at the expense of TeO$_4$ units. **Fig. 5.17** displays the intensity variation of Raman bands in niobium tellurite glasses.

An additional band at 876 cm$^{-1}$ in niobium tellurite glasses is observed, along with the five other bands at 455 cm$^{-1}$, 610 cm$^{-1}$, 660 cm$^{-1}$, 712 cm$^{-1}$, 769 cm$^{-1}$, which are the characteristics of normal TeO$_2$ Raman modes, as reported by various authors [Sekiya et al. (1989); Sekiya et al. (1994)]. The band at 871- 876 cm$^{-1}$ region of the Raman spectra can be assigned to the bending modes of Nb-O-Nb bonds found in NbO$_6$ octahedra and symmetrical stretching vibrations of Nb-O bonds in NbO$_6$ octahedra. Existence of this peak confirms the presence of NbO$_6$ octahedra in these glasses and the slight increase in intensity of this band confirms the increase in the concentration of NbO$_6$ octahedra with Nb$_2$O$_5$ content [Babu and Mouli (2009)]. The increase in NbO$_6$ octahedra with the increase in Nb$_2$O$_5$ content increases the internetworking of TeO$_4$ units and connects the Te-O chains in glass network, thereby makes the network more rigid. This result is consistent with increase in glass transition temperature and increase in oxygen packing density. The band at 800-900 cm$^{-1}$ is also observed by Fukumi and Sakka in niobate crystals which are again assigned to NbO$_6$ octahedra with NBOs and/or with much distortion [Fukumi and Sakka (1989)].

![Fig. 5.17 Intensity variation of Raman bands with Nb$_2$O$_5$ concentration (mol%).](image)
Murugan and Ohishi studied 20Nb₂O₅-80TeO₂, 10Nb₂O₅-80TeO₂-10TiO₂, 10SrO-90TeO₂ and ZnO-Na₂O-TeO₂ glasses, and found that the Raman band at 850 cm⁻¹ was found only in first two glasses, which contains Nb₂O₅, whereas the other two glasses did not show this band, since this band was the feature of vibration in Nb and its neighbouring NBO in NbO₆ octahedra [Murugan and Ohishi (2004)]. Table 5.6 shows the assignment of Raman band frequencies of niobium tellurite glasses. The ratio of concentration of TeO₃ and TeO₄ structural units in niobium tellurite glasses is calculated by adopting a procedure proposed by Kalampounias et al. [Kalampounias et al. (2007); Kalampounias et al. (2011)]. In this method, the relative amount of TeO₃ (tp) and (TeO₄) tbp units is estimated by calculating the ratio of intensities of the Raman bands at 769 cm⁻¹ and 660 cm⁻¹, respectively, which is considered proportional to the concentration ratio R, where R= [TeO₃] / [TeO₄] of these units. The intensity ratio, I₇₆₉/I₆₆₀ increases from 0.34 to 0.43 as Nb₂O₅ concentration is varied from 5 to 20-mol%, indicating the increase in concentration of TeO₃ units at the expense of TeO₄ structural units. FTIR studies by earlier authors also reported the increase in concentration of TeO₃ units with increase in Nb₂O₅ concentration in binary niobium tellurite glasses [Lin et al. (2009)].

Table 5.6 Raman bands assignment of deconvoluted Raman spectra of normal and splat-quenched niobium tellurite glasses.

<table>
<thead>
<tr>
<th>Raman band frequencies (cm⁻¹)</th>
<th>Vibrational mode assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>454-455</td>
<td>Symmetric stretching and bending vibrations of Te-O-Te linkages</td>
</tr>
<tr>
<td>609-612</td>
<td>Te-O bond stretching vibrations of TeO₄ units</td>
</tr>
<tr>
<td>660-664</td>
<td>Te-O bond stretching vibrations of TeO₃ units</td>
</tr>
<tr>
<td>710-713</td>
<td>Te-O bond stretching vibrations of TeO₃ units</td>
</tr>
<tr>
<td>769-771</td>
<td>Te-O bond stretching vibrations of TeO₃ units</td>
</tr>
<tr>
<td>871-876</td>
<td>Bending modes of Nb-O-Nb bonds found in NbO₆ octahedra and symmetrical stretching vibrations of Nb-O bonds in NbO₆ octahedra</td>
</tr>
</tbody>
</table>
An abrupt increase in intensity ratio (16%) is observed when Nb$_2$O$_5$ increases from 5 to 10 mol% and then a comparatively smaller increase in intensity ratio is observed (8%) when Nb$_2$O$_5$ is increased from 10 to 15 mol% and later saturation effects are observed when Nb$_2$O$_3$ is increased beyond 15 mol%. Fig. 5.18 displays the variation of intensity ratio with Nb$_2$O$_5$ concentration in niobium tellurite glasses.

**Fig. 5.18** Variation of intensity ratio, $I_{769}/I_{660}$ with Nb$_2$O$_5$ concentration.

This indicates that significant changes occur in the structure of glasses when Nb$_2$O$_5$ concentration is increased from 5 to 15- mol%, and further addition of Nb$_2$O$_5$ beyond 15- mol% produces smaller changes in the structure of glasses.
Summary

Niobium tellurite glasses of composition xNb$_2$O$_5$-(100-x)TeO$_2$ with x= 5, 10, 15 and 20 mol% are prepared and characterized by XRD, density, UV-visible absorption spectroscopy, DSC and Raman spectroscopy. Low temperature specific heat capacity measurements are carried out and the characteristics of boson peak are studied.

Density decreases from $5.533 \pm 0.003 \text{ g cm}^{-3}$ to $5.229 \pm 0.002 \text{ g cm}^{-3}$, in normally quenched niobium tellurite glasses and in splat-quenched glasses decreases from $5.512 \pm 0.028 \text{ g cm}^{-3}$ to $5.225 \pm 0.010 \text{ g cm}^{-3}$ with the increase in Nb$_2$O$_5$ concentration from 5 to 20 mol %. Molar volume increases significantly from 29.81 cm$^3$ mol$^{-1}$ to 34.59 cm$^3$ mol$^{-1}$ in normal-quenched glasses. Similar trend in molar volume is observed in splat-quenched glasses.

The increase in Nb$_2$O$_5$ concentration generates free volume or voids in the glass network, which cause the decrease in glass density and the increase in molar volume. Oxygen packing density (OPD) increases from 72.14 g atom liter$^{-1}$ to 75.18 g atom liter$^{-1}$ in normal quenched glasses while in splat quenched glasses, it increases from 71.86 g atom liter$^{-1}$ to 75.12 g atom liter$^{-1}$.

The optical cut off wavelength increases slightly from 395 nm to 402 nm with the increase in Nb$_2$O$_5$ concentration from 5 to 20 mol%. Niobium tellurite glasses show an intense optical band just below the absorption cut-off in the wavelength range of 394-400 nm which can be due to the electronic excitations of Nb$^{5+}$ ions or even due to lone pair of electrons on Te atoms.

Glass transition temperature increases from 330°C to 416°C with the increase in Nb$_2$O$_5$ concentration from 5 to 20 mol%, and is due to higher bond strength of Nb-O bond (bond enthalpy = 752.4 kJ/mol) than Te-O (bond enthalpy=376 kJ/mol) bond. The increase in Nb$_2$O$_5$ concentration increases the rigidity and homogeneity of glass network due to the increased linkages by NbO$_6$ octahedra, and at higher Nb$_2$O$_5$ mol%, only one crystalline phase, Nb$_2$Te$_3$O$_{13}$ is formed.
Low-temperature specific heat capacity measurements found that with the increase in the concentration of Nb\textsubscript{2}O\textsubscript{5} from 5 to 20 mol\%, the maxima in C\textsubscript{p}/T\textsuperscript{3} decreases from 6.43 J mol\textsuperscript{-1}K\textsuperscript{-2} to 5.48 J mol\textsuperscript{-1}K\textsuperscript{-2} and the temperature of maxima increased from 9.06K to 10.88K. The addition of Nb\textsubscript{2}O\textsubscript{5} strengthens and homogenizes the tellurite glass network.

Raman study showed that Nb\textsubscript{2}O\textsubscript{5} acts as a modifier in the molar concentration range of 5 to 20-mol\%. The intensity ratio, I\textsubscript{769}/I\textsubscript{660} increases from 0.34 to 0.43 with the increase in Nb\textsubscript{2}O\textsubscript{5} concentration from 5 to 20-mol\%, indicating the increase in concentration of TeO\textsubscript{3} units at the expense of TeO\textsubscript{4} structural units. The increase in intensity of 871-876 cm\textsuperscript{-1} band confirms the increase in the concentration of NbO\textsubscript{6} octahedra with Nb\textsubscript{2}O\textsubscript{5} which enhances the internetworking of TeO\textsubscript{4} units and connects the Te-O chains in glass network, thereby makes the network more rigid.
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Kalampounias, A. G., Nasikas, N. K. and Papatheodorou, G. N. (2011). Structural investigations of the xTeO$_2$-(1-x)GeO$_2$ (x= 0, 0.2, 0.4, 0.6, 0.8 and 1) tellurite glasses: A composition dependent Raman spectroscopic study. *Journal of Physics and Chemistry of Solids* **72**: 1052-56.


