Infrared, ESR and optical absorption studies of Cu$^{2+}$ ions doped in TeO$_2$-ZnO-NaF glass system

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Glasses of composition $80$TeO$_2$-(20−$x$)ZnO-$x$NaF mol % were prepared by melt quenching technique and characterized by ESR, optical absorption and infrared spectroscopy. The IR spectra reveal that the glass consists of TeO$_3$, TeO$_4$, Te(O,F)$_3$ and Te(O,F)$_4$ units as local structure of the glass network. The hydroxyl group concentration decreases with the increase of NaF content. From ESR spectra, it is found that the Cu$^{2+}$ ions are in octahedral sites with tetragonal distortion with $d_{x^2-y^2}$ as ground state. From the ESR and optical absorption studies, molecular orbital coefficients were calculated and correlated with the structural variation of the glass system. From the optical absorption data, the optical band gap ($E_{opt}$) and Urbach energy ($\Delta E$) values were calculated. It is found that $E_{opt}$ values increase with NaF content. The low $\Delta E$ values showed that the present glasses were highly homogenous and stable.

Keywords: Tellurite glasses, Infrared spectroscopy, ESR, Optical absorption, Cu$^{2+}$ ions

1 Introduction

In recent years, heavy metal oxide and oxyfluoride glasses have received considerable attention for their potential applications in fiber lasers for mid IR-region and non-linear optics$^1$. The tellurite glasses have been extensively investigated over two decades, due to their optical properties like high refractive index and high transmittance in near IR region$^1$.

These glasses are characterized by good chemical durability, good thermal stability and high solubility of rare-earth ions$^1$. On the other hand, fluoride glasses have lower phonon energy with a broader optical transmittance region$^2,3$ between 0.3 and 7 $\mu$m. It requires a more complex fabrication route than tellurite glasses. The chemical interaction between fluorine and hydroxyl ions decreases the unwanted hydroxyl concentration which subsequently reduces the optical absorption loss in IR region as well as the quenching effect on the excited levels of rare-earth ions$^4$.

A number of papers have been published on alkali-fluoro borate and alkali-tellurite glass systems, for example Shelby and Ortolano$^5$ prepared NaF-Na$_2$O-B$_2$O$_3$ glass system and studied the refractive index, density and glass transition temperature of all glasses. Karthikeyan and Mohan$^6$ had prepared and investigated the structural, glass transition and optical properties of Nd$^{3+}$ doped NaF-Na$_2$O-B$_2$O$_3$ glasses of different compositions. The structural and optical properties of alkali-fluoro borate glass system B$_2$O$_3$-XCO$_3$-NaF-Eu$_2$O$_3$ (X = Li$_2$, Na$_2$, Ca and Mg) were studied by Marimutha et al$^7$. Guhua et al.$^8$ prepared a new fluoro tellurite glass system, (85−$x$)TeO$_2$-$x$ZnF$_2$-12PbO-3Nb$_2$O$_5$ ($x = 0$ to 40), for photonic applications.

In this paper, infrared, ESR and optical absorption studies of $80$TeO$_2$-(20−$x$)ZnO-$x$NaF glass system have been studied. The effect of fluorine ions on the Te-O stretching vibrations in TeO$_4$ and TeO$_3$ groups and on the stretching vibrations of hydroxyl group O-H has been investigated. The effect on the structural changes, spin-Hamiltonian parameters, bonding parameters and optical band gap values has also been studied.

2 Experimental Details

Glass samples of composition $80$TeO$_2$-(20−$x$) ZnO-$x$NaF, $x = 0, 5, 10, 15$ and $20$ mol % were prepared by melt quenching technique with compositions as presented in Table 1. The starting materials (Sigma Aldrich Chemicals with 99.99% purity) are NaF, ZnO, TeO$_2$ and CuO. The chemicals were weighed accurately in an electronic balance mixed thoroughly and ground to fine powder. The batches were placed in platinum crucible and melted in an electric furnace at 800$^\circ$C for 30 min. The melt was then quenched in air at room temperature by pouring it onto a polished brass plate and pressing quickly with another brass
plate. Green coloured glasses are obtained which have good optical quality and good transparency. Glass samples are annealed at 150°C for 6 h in order to relieve stress and strains. The glasses are named as NZT1, NZT2, NZT3, NZT4 and NZT5 for \( x = 0, 5, 10, 15 \) and 20, respectively and are presented in Table 1.

The amorphous nature of glass samples were confirmed by XRD using a copper target (\( K_{α} = 1.54\)Å) on Phillips PW1140 diffractometer at room temperature. Electron spin resonance spectra of all glass samples were recorded by using JEOL-JMFe3, ESR spectrometer operating at X-band with 100 kHz field modulation at room temperature. IR transmission spectra of glass samples were recorded using Perkin-Elmer FT-IS Spectrophotometer model 1605 in wavenumber range 400-4000 cm\(^{-1}\) at room temperature. Optical absorption spectra of samples of about 1 mm thickness were recorded with Shimadzu UV-3100 Spectrometer in the wavelength range 400-900 nm at room temperature taking air as reference medium. The peak pick facility provided in spectrophotometer was utilized to measure the peak position.

### Results and Discussion

#### 3.1 XRD and IR spectra

The X-ray diffraction spectra show no sharp peaks which indicate amorphous nature of glass samples. IR spectra give information about the specific structural units present in the glass system. IR spectra of NaF-ZnO-TeO\(_2\) glasses (NZT1, NZT2, NZT3, NZT4 and NZT5) are shown in Fig. 1.

Transmission spectra of all glasses accumulated in three different regions 3600-2100, 650-780 cm\(^{-1}\) and around 1120 cm\(^{-1}\). In Fig. 1, NZT1 glass absorption bands are located around 3450, 3100, and 2300 cm\(^{-1}\). These bands are due to the small amount of atmospheric water present in spectrophotometer or it may be due to the hydrolyzation of glass melt by furnace atmosphere. The more intense band around 3450 cm\(^{-1}\) is attributed to the stretching mode of free Te-OH groups. The less intense band around 3100 cm\(^{-1}\) is ascribed to the stretching mode of weak hydrogen bond.

Te-OH groups and less intense band around 2300 cm\(^{-1}\) are due to the stretching mode of strong hydrogen bonded Te-OH groups. In the glass system TeO\(_2\)-ZnF\(_2\)-Na\(_2\)O, O’Donnell’s et al. suggested that the absorption band around 3300 cm\(^{-1}\) is due to the stretching mode of free Te-OH groups, absorption band around 3060 cm\(^{-1}\) is attributed to the stretching mode of weak hydrogen bonded Te-OH groups and absorption band located around 2290 cm\(^{-1}\) is due to the stretching mode of strongly hydrogen bonded Te-OH groups. In NaF-Na\(_2\)O-B\(_2\)O\(_3\) system, a broad absorption band around 3440 cm\(^{-1}\) is attributed to the hydroxyl group stretching vibrations by Karthikeyan et al. and Nazabal et al. investigated that the absorption band around 3600 cm\(^{-1}\) is due to stretching mode of hydroxyl groups.

In alkali-silicate glasses Scholze found an absorption band around 3500 cm\(^{-1}\), which is attributed to stretching mode of free Si-OH groups and band at 2350 cm\(^{-1}\) is due to stretching mode of strong hydrogen bonded Te-OH groups. Ryskin and Ryskin recognized a band around 3500 cm\(^{-1}\) in hydrated crystalline silicates which is attributed to stretching mode of water molecule. So we can propose that bands around 2300, 3100 and 3450 cm\(^{-1}\) are due to stretching mode of strong hydrogen bonded Te-OH groups, weak hydrogen bonded Te-OH groups and free Te-OH groups, respectively.

As shown in Fig. 1, absorption band intensity around 3450 cm\(^{-1}\) is gradually decreases with increase of NaF content. This is due to the decrease in the hydroxyl group concentration with increase of NaF content.

### Table 1—Composition of 80 TeO\(_2\)-(20-x)ZnO-xNaF glass system

<table>
<thead>
<tr>
<th>Glass code</th>
<th>Composition (mole%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TeO(_2)</td>
</tr>
<tr>
<td>NZT1</td>
<td>80</td>
</tr>
<tr>
<td>NZT2</td>
<td>80</td>
</tr>
<tr>
<td>NZT3</td>
<td>80</td>
</tr>
<tr>
<td>NZT4</td>
<td>80</td>
</tr>
<tr>
<td>NZT5</td>
<td>80</td>
</tr>
</tbody>
</table>
The decrease in the hydroxyl group concentrations can be attributed to the volatilization of batch material, because at high temperature fluorine\(^{14}\) readily reacts with water in melt and in furnace atmosphere producing HF.

In Fig. 1, absorption bands for NZT1 are observed around 770 and 650 cm\(^{-1}\). The absorption bands around 770 and 650 cm\(^{-1}\) are due to the Te-O vibration in TeO\(_3\) and TeO\(_4\), respectively. One more absorption band identified around 1120 cm\(^{-1}\) is attributed to the Te-O-Zn linkages\(^{15}\). In NZT1 glass, a small absorption band appeared around 460 cm\(^{-1}\), which can be attributed to Zn-O linkages\(^{15}\).

In glasses from NZT2 to NZT5, the absorption band around 650 cm\(^{-1}\) gradually shifts towards higher wavenumbers. This is attributed to the decrease of TeO\(_4\) units, with the formation of TeO\(_3\) and TeO\(_3\) (or) Te(O,F)\(_3\) units in fluorotellurite glasses. This change in the glass structure is due to the breakage effect of F\(^{-}\) ions on Te-O-Te and Te-O-Zn linkages\(^{15}\).

Hence, from studies on fluorotellurite glasses\(^{10,25,26}\), it can be inferred that in the present glass system the fluorine F\(^{-}\) substitutes O\(^{2-}\) ions in TeO\(_4\) units resulting the formation of Te(O,F)\(_3\) units and the conversion of Te(O,F)\(_4\) units into Te(O,F)\(_3\) units with the increase of NaF content.

### 3.2 ESR studies

Electron Spin Resonance is used to characterize the local structure of a para-magnetic centre. ESR can interpret observed transitions among various energy levels, structural and chemical environment about the metal ion. The ESR spectrum exhibits resonance signals similar to those reported in earlier studies\(^{27-32}\).

Cu\(^{2+}\) ions with S=1/2 has a nuclear spin I=3/2 for both \(^{63}\)Cu (natural abundance of 69\%) and \(^{65}\)Cu (natural abundance of 31\%) and therefore (2I+1) i.e., four parallel and four perpendicular components would be expected.

Figure 2 shows the typical ESR spectra of glass samples. The spin-Hamiltonian parameters are calculated from the spectra by using the equation given by Dance et al.\(^{33}\) and are presented in Table 3. For Cu\(^{2+}\) ions, a regular octahedral site may not exist because tetragonal distortion is produced by an electron hole in the degenerate \(d_{x^2-y^2}\) orbital which is in cubic symmetry. The ESR spectra of glass samples are analyzed by using an axial spin-Hamiltonian of the form\(^{34}\).

#### Table 2—Peak frequencies of IR in 80TeO\(_2\)-(20-x)ZnO-xNaF glass system

<table>
<thead>
<tr>
<th>Glass sample</th>
<th>Peak positions (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>NZT1</td>
<td>460 650 770 3450</td>
</tr>
<tr>
<td>NZT2</td>
<td>460 658 772 3300</td>
</tr>
<tr>
<td>NZT3</td>
<td>460 663 775 3100</td>
</tr>
<tr>
<td>NZT4</td>
<td>460 670 778 —</td>
</tr>
<tr>
<td>NZT5</td>
<td>— 690 780 —</td>
</tr>
</tbody>
</table>

#### Table 3—Spin-Hamiltonian parameters of Cu\(^{2+}\) ions in 80TeO\(_2\)-(20-x)ZnO-xNaF glass system

<table>
<thead>
<tr>
<th>Glass sample</th>
<th>(g_\parallel)</th>
<th>(g_\perp)</th>
<th>(A_\parallel(\times 10^{-3}) cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>NZT1</td>
<td>2.365</td>
<td>2.134</td>
<td>118</td>
</tr>
<tr>
<td>NZT2</td>
<td>2.354</td>
<td>2.127</td>
<td>120</td>
</tr>
<tr>
<td>NZT3</td>
<td>2.361</td>
<td>2.131</td>
<td>116</td>
</tr>
<tr>
<td>NZT4</td>
<td>2.357</td>
<td>2.131</td>
<td>116</td>
</tr>
<tr>
<td>NZT5</td>
<td>2.362</td>
<td>2.134</td>
<td>117</td>
</tr>
</tbody>
</table>
\[ H = g_{11} \beta H_z S_z + g_{21} \beta (H_x S_x + H_y S_y) + A_{11} S_z I_z + A_{21} (S_x I_x + S_y I_y) \]  

(1)

Here, 'z' is the symmetry axis of individual Cu\(^{2+}\) ions, \( \beta \) is Bohr magneton, \( A_{1} \) and \( A_{2} \) are the parallel and perpendicular components of the hyperfine coupling tensor 'A', \( g_1 \) and \( g_\perp \) are parallel and perpendicular components of 'g' tensor. \( H_x \), \( H_y \) and \( H_z \) are the components of magnetic field. \( S_x \), \( S_y \) and \( S_z \) are components of spin operators of the electron and \( I_x \), \( I_y \) and \( I_z \) are the spin operators of the nucleus.

In Fig. 2, ESR spectra show the parallel and perpendicular hyperfine lines. The solution of the spin Hamiltonian gives the expressions for the peak positions related to the principal 'g' and 'A' tensors as:

\[ h\nu = g_{11} \beta B + mA_1 + \left[ \frac{15}{4} - m^2 \right] \frac{A_1^2}{2g_{11} \beta B} \]  

(2)

\[ h\nu = g_\perp \beta B + mA_\perp + \left[ \frac{15}{4} - m^2 \right] \frac{A_1^2 + A_\perp^2}{4g_\perp \beta B} \]  

(3)

Here, \( m \) is the nuclear magnetic quantum number of Cu nucleus with values 3/2, 1/2, -1/2 and -3/2. And '\( \nu \)' is micro wave frequency at resonance. By using Eqs 2 and 3, spin Hamiltonian parameters are calculated and presented in Table 3. From Table 3, it is clear that the spin Hamiltonian parameters are varying with \( x \). The observed \( g_1 \) and \( g_\perp \) values are characteristic of Cu\(^{2+}\) ions coordinated by six ligands which form the complex elongated along z-axis and as \( g_1 > g_\perp \), the ground state of Cu\(^{2+}\) ions is \( d_{x^2-y^2} \) (\( ^2B_{1g} \) state).

Moreover, \( g_6 \), \( g_\perp \) and \( A_\parallel \) values are continuously changing with respect to the NaF concentration. The \( g_1 \) values are maximum for 20 mol% of NaF. The \( g_\perp \) value decreases upto 5 mol % and increases with addition of NaF upto 20 mol %. All values are also continuously varying with NaF concentration. This continuous variation of \( g_6 \), \( g_\perp \) and \( A_\parallel \) values indicates the distortion around the Cu\(^{2+}\) ions is changing with NaF content, which suggests that continuous structural changes are taking place in the glass system.

These structural changes agree with IR spectral data, where the partial conversion of TeO\(_3\) units into TeO\(_2\) units takes place with the addition of NaF content. The observed changes in the Hamiltonian parameters are in good agreement with the earlier ESR studies on oxide glass system \(^{34-36}\).

### 3.3 Optical absorption studies

Figure 3 shows the optical absorption spectra of 1 mol% of Cu\(^{2+}\) ions doped 80 TeO\(_2\)-(20-x)ZnO-xNaF (5 \( \leq x \leq 20 \)) glass system. It is clearly indicating a broad absorption band centered around 810 nm. This band is assigned to the transitions of Cu\(^{2+}\) ions from \( ^2B_{1g} \rightarrow ^2B_{2g} \) in a distorted octahedral site \(^{36-38}\). The cubic symmetry of Cu\(^{2+}\) ions is disturbed by electronic hole in the degenerate orbital which causes the tetragonal distortion. According to Jahn-Teller theorem, any non-linear system with a degenerate ground state should distort in order to eliminate the degeneracy. So, two structural changes may be possible, one is elongated and another one is compressed structure. In these glass systems, Cu\(^{2+}\) ions are in octahedral symmetry with elongated tetragonal distortion.

#### 3.3.1 Molecular orbital coefficients

The bonding coefficients are evaluated by correlating the EPR and optical absorption data as follows \(^{39}\):

\[ g_{11} = 2.0023 \left[ 1 - \frac{4\lambda \alpha^2 \beta_2^2}{\Delta E_{xy}} \right] \]  

(4)

\[ g_\perp = 2.0023 \left[ 1 - \frac{\lambda \alpha^2 \beta_2^2}{\Delta E_{x_{yz}}} \right] \]  

(5)

where, \( \lambda (=828 \text{ cm}^{-1}) \) is spin orbit coupling constant for Cu\(^{2+}\) ions and \( \beta_2^2 \approx 1 \) for octahedral environment. \( \Delta E_{xy} \) and \( \Delta E_{x_{yz}} \) are the heights of the \( d_{x^2-y^2} \) and \( d_{x_{yz}} \) molecular orbital levels above the ground state \( d_{x^2-y^2} \), respectively and these values are estimated from optical absorption spectra \(^{40}\). In optical absorption spectra, the position of observed absorption maximum of Cu\(^{2+}\) ions indicates the values of \( \Delta E_{xy} \). The frequency position \( \Delta E_{x_{yz}} \) depends on the assumption that for
Cu$^{2+}$ ions in distorted octahedral environment and is calculated by $\Delta E_{xx,yy} = 2k^2\lambda/(2.002-g_\perp)$.

The parameters $\alpha^2$ and $\beta_i^2 (\approx 1)$ represent the contribution of 3d atomic orbital of cupric ion to the $B_{1g}$ and $B_{2g}$ anti bonding orbital, respectively.

The bonding coefficient $\alpha^2$ can be calculated from the ESR data by using the expression given by Kuska et al.$^{41}$.

$$\alpha^2 = \frac{7}{4} \frac{A_{11}}{P} \left( \frac{A}{P} - \frac{2}{3} g_{11} - \frac{5}{21} g_{\perp} + \frac{6}{7} \right) \quad \ldots(6)$$

$$\beta_i^2 = \left[ \frac{g_{\perp} - 1}{g_c} \right] \frac{\Delta E_{xx,yy}}{828\alpha^2} \quad \ldots(7)$$

where $P = 0.036$ cm$^{-1}$, $A = (1/3 A_0 + 2/3 A_\perp)$ and $\Delta E_{xx,yy} = 2k^2\lambda/(2.002-g_\perp)$, $k$ is the orbital reduction factor, $k^2 = 0.77$.

The bonding coefficients $\alpha^2$, $\beta_1^2$, $\beta_2^2 (= 1.00)$ characterize in-plane-$\sigma$ bonding, in-plane $\pi$ bonding and out-of-plane $\pi$ bonding of Cu$^{2+}$ ligand bond in glasses, respectively. The values of these parameters lie between 0.5 and 1.0. If $\alpha^2 = 1$, the bond would be purely ionic, and if $\alpha^2 = 0.5$, the bond would be completely covalent. The normalized covalency of Cu (II)-O in plane $\sigma$ and $\pi$ bondings is expressed in terms of bonding coefficients $\alpha^2$ and $\beta_i^2$ as follows:

$$\Gamma_\sigma = \frac{200(1-S)(1-\alpha^2)}{1-2S} \quad \% \quad \ldots(8)$$

$$\Gamma_\Pi = \frac{200(1-\beta_i^2)}{3} \quad \% \quad \ldots(9)$$

'S' is the overlap integral ($S_{\text{oxygen}} = 0.076$).

The molecular orbital bonding coefficients and covalency are calculated and presented in Table 4. From Table 4, it is clear that for all glasses one broad absorption band is observed around 810 nm. This has been attributed to the $^2B_{1g} \rightarrow ^2B_{2g}$ transition of Cu$^{2+}$ ions in a distorted octahedral site. The peak positions for the different glasses are presented in Table 4. The peak position values are shifted towards higher wavelengths with increase of the concentration of NaF upto 10%. Then, peak position is shifted towards lower wavelengths with the increase of NaF concentration from 15 to 20%. The peak position reaches maximum for 10 mol % of NaF concentration. This continuous variation in peak position shows the variation in the ligand field around Cu$^{2+}$ ions, which represents change in polarizability of oxygen ions surrounding the Cu$^{2+}$ ions and its dependence on field strength of network formers.

Table 4 — Molecular Orbital Bonding Coefficients and covalency of Cu$^{2+}$ doped 80TeO$_2$-(20-x)ZnO-xNaF glass system

<table>
<thead>
<tr>
<th>Glass sample</th>
<th>Cu$^{2+}$ peak (nm)</th>
<th>$\alpha^2$</th>
<th>$\beta_1^2$</th>
<th>$\beta_2^2$</th>
<th>$\Gamma_\sigma$</th>
<th>$\Gamma_\Pi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NZT1</td>
<td>810</td>
<td>0.7907</td>
<td>0.9726</td>
<td>0.8549</td>
<td>45.61</td>
<td>29.02</td>
</tr>
<tr>
<td>NZT2</td>
<td>813</td>
<td>0.7818</td>
<td>0.9836</td>
<td>0.8339</td>
<td>47.53</td>
<td>33.22</td>
</tr>
<tr>
<td>NZT3</td>
<td>815</td>
<td>0.7782</td>
<td>0.9854</td>
<td>0.8505</td>
<td>48.31</td>
<td>29.90</td>
</tr>
<tr>
<td>NZT4</td>
<td>805</td>
<td>0.7753</td>
<td>0.9921</td>
<td>0.8562</td>
<td>48.95</td>
<td>28.76</td>
</tr>
<tr>
<td>NZT5</td>
<td>804</td>
<td>0.7745</td>
<td>0.9934</td>
<td>0.8554</td>
<td>49.01</td>
<td>27.92</td>
</tr>
</tbody>
</table>

This study $\alpha^2$, $\beta_1^2$, $\beta_2^2$ values are near to one, so the glass system is ionic in nature. These structural changes are correlated with IR results where partial conversion of TeO$_4$ units into TeO$_3$ units with the increase of NaF content is taking place.

3.3.2 Optical energy gap and Urbach energy

Generally, optical absorption in solids and liquids occur by various mechanisms, in all of which the photon energy will be absorbed by either the lattice or by electrons where the transferred energy is conserved. The lattice absorption will give information about the atomic vibrations involved. The higher energy parts of spectrum particularly those associated with the inter band electronic transition will provide the information about electron states. In this process, the electrons are excited from filled to an empty band by the photon absorption, as a consequence a sharp increase in absorption coefficient $\alpha(\omega)$ will result. The onset of this rapid change in $\alpha(\omega)$ is called the fundamental absorption edge and corresponding energy is defined as optical energy gap, $E_{\text{opt}}$. The general formula for absorption coefficient $\alpha(\omega)$ is given by:

$$\alpha(\omega) = \frac{1}{L} \ln \frac{I_0}{I_1} \quad \ldots(10)$$

where $I_0$ and $I_1$ are the intensity of incident and transmitted light, respectively, and $L$ is the thickness of the sample.

The optical energy gap can be determined by the Davis and Mott’s relation$^{42}$:

$$\alpha \omega = A(\hbar \omega - E_{\text{opt}})^n \quad \ldots(11)$$

where $A$ is a constant, $\alpha$ is the absorption coefficient and $n$ is an index which takes the values of 2, 1/2, 3, 3/2 for indirect, direct, direct forbidden and indirect forbidden transitions, respectively. Here $n = 2$ is found to represent the experimental results and this applies to indirect allowed transition.
A plot of $\rho \nu$ versus $(\alpha \rho \nu)^{1/2}$ is drawn as shown in Fig. 4. The optical energy gap value for prepared glasses was determined by extrapolating the linear regions of the curves. In forbidden energy band gap, a band tailing occurs for amorphous materials. The extent of this band tailing is the measure of degree of disorder in the material. The width of band tails of the electron states can be estimated by Urbach equation 

$$\Delta \omega = \omega \alpha \exp(\frac{-\omega}{B})$$  \hspace{1cm} ...(12) 

where $B$ is a constant, $\Delta \omega$ is the width of band tails of electron states also known as Urbach energy. glass system

Figure 5 shows a plot between $\rho \nu$ and $\ln(\alpha)$. The slope of this graph gives Urbach energy. For the prepared glasses, optical band gap and Urbach energy are calculated and presented in Table 5.

From Table 5, it is clear that the optical band gap values are increasing with NaF content from 2.44 to 2.60 eV. Urbach energy values lie between 0.69 and 0.75 eV. These small values of Urbach energy indicate that the present glass system is highly homogeneous and stable. In this system, optical band gap increases with NaF content, it may be due to the strong influence of F ion on Te-O bonds in tellurite glass network.

### 4 Conclusions

From the IR spectra, it is clear that the glass system contains two types of structural groups, trigonal pyramid TeO$_3$, Te (O,F)$_3$ and tetragonal bipyramid (TeO$_4$) and continuous conversion of TeO$_4$ into TeO$_3$ units takes place with the increase of NaF content. A broad band observed around 3360 cm$^{-1}$ is the band due to hydroxyl group. The intensity of the hydroxyl group decreases with the addition of NaF content which may be useful in IR lasers. From the spin-Hamiltonian parameters of Cu$^{2+}$ ions in present glasses, it is found that $g_1 > g_4$, which indicates that Cu$^{2+}$ ions are present in octahedral sites with tetragonal distortion. Optical absorption spectra in all glasses show a single broad band around 810 nm which is due to the transition of Cu$^{2+}$ ions from $^2B_1g \rightarrow ^2B_2g$ state. The molecular orbital coefficients $\alpha_2$, $\beta_1$, $\beta_2$ evaluated by correlating Cu$^{2+}$ ions from $^2B_1g \rightarrow ^2B_2g$ state. The molecular orbital coefficients depend on the NaF content. i.e., alkali content causes continuous structural changes in the

<table>
<thead>
<tr>
<th>Glass code</th>
<th>Sample thickness (±0.01) (mm)</th>
<th>Optical band gap (±0.01) (eV)</th>
<th>Urbach energy (±0.01) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NZT1</td>
<td>1.21</td>
<td>2.44</td>
<td>0.75</td>
</tr>
<tr>
<td>NZT2</td>
<td>1.20</td>
<td>2.49</td>
<td>0.69</td>
</tr>
<tr>
<td>NZT4</td>
<td>1.19</td>
<td>2.55</td>
<td>0.71</td>
</tr>
<tr>
<td>NZT5</td>
<td>1.21</td>
<td>2.60</td>
<td>0.73</td>
</tr>
</tbody>
</table>
glass structure. The optical band gap values are determined from optical absorption spectra which are in the range 2.44-2.60 eV. The increase in optical band gap values may be assigned to the strong influence of F ion on Te-O bond and almost equal atomic radii of fluorine and oxygen. The smaller values of Urbach energy indicate that the present glass system is highly homogeneous and stable.

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