Spectroscopic Properties of alkaline earth bismuth borate glasses doped with TiO$_2$

4.1 Introduction:

Among various transition metal ions, doping of TiO$_2$ to alkaline earth bismuth borate glass augments the applications of base glass due to the similar advantages of TiO$_2$, such as high transparency in the visible to near-infrared wavelength region, high refractive index [1] with bismuth borate glasses. Generally, in the glass matrix titanium ions exists in Ti$^{4+}$ state with TiO$_4$, TiO$_6$ and sometimes with TiO$_5$ (comprising of trigonal bipyramids) structural units. Murali Krishna et al [2] observed that during melting process some of Ti$^{4+}$ ions might be reduced into Ti$^{3+}$ valence state in certain glass matrices and acts as modifiers. As a consequence of such variation in coordination and valence of titanium ions in the glass network produces structural modification and local-field variation in the structure which influences its potential applications.

The presence of Ti$^{4+}$ ions makes glass to be suitable for non-linear optical devices, since the empty or unfilled d-shells of these ions contribute more strongly to nonlinear polarizabilities. Usually, the d-orbital contribution to non-linear polarizability is found to be more for bond lengths less than 2 Å; the bond length of Ti-O is estimated to be 1.96 Å. Literature survey on the glasses containing TiO$_2$ indicates that these glasses possess negative non-linear refractive index that induces self-focusing radiation beam in the material; as a result, the devices can be operated at a smaller input power. Nevertheless, the investigation on the co-ordinate chemistry of Ti$^{4+}$ and Ti$^{3+}$ ions in Bi$_2$O$_3$–B$_2$O$_3$ glass network is of interest itself because, these ions are expected to
influence the structural properties of the glasses to a large extent. By keeping the potential applications of titanium ions doped glasses in view, in the present chapter six samples of composition 10MO.20Bi$_2$O$_3$.($70-x$)B$_2$O$_3$.xTiO$_2$, [R=Ca, Sr] with x=0, 0.5, 1.0 (Wt%) were prepared and their specific spectroscopic properties we studied. Fig. 4.1 represents the physical appearance of 2 mm thick samples. The details of composition are as follows:

CT$_0$: 10CaO-20Bi$_2$O$_3$-70.0B$_2$O$_3$

CT$_{05}$: 10CaO-20Bi$_2$O$_3$-69.5B$_2$O$_3$-0.5TiO$_2$

CT$_{10}$: 10CaO-20Bi$_2$O$_3$-69.0B$_2$O$_3$-1.0TiO$_2$

ST$_0$: 10SrO-20Bi$_2$O$_3$-70.0B$_2$O$_3$

ST$_{05}$: 10SrO-20Bi$_2$O$_3$-69.5B$_2$O$_3$-0.5TiO$_2$

ST$_{10}$: 10SrO-20Bi$_2$O$_3$-69.0B$_2$O$_3$-1.0TiO$_2$

![Fig. 4.1 Physical appearance of 2.0 mm thick TiO$_2$ doped glass samples.](image)

**4.2 Brief review on the literature of TiO$_2$ doped materials:**

Srinivasa Rao et al [3] studied the dielectric and spectroscopic properties of TiO$_2$ mixed lithium aluminium zirconium silicate glasses and observed that with increase in titanium content in the glass matrix visible luminescence efficiency is increased and octahedral Ti$^{4+}$ ions are responsible for such luminescence emission. Besides, dielectric parameters are observed to decrease with increase in TiO$_2$ due to increased proportion of Ti$^{4+}$ ions in network forming positions rather than interstitial
spaces and some of Ti$^{4+}$ ions are found to reduce to Ti$^{3+}$ ions in the glass matrix. Lebedev et al [4] produced TiO$_2$ doped silica host glasses with laser torch technique and investigated the luminescence, Raman and ESR spectroscopy. They observed a luminescence due to oxygen deficient centers produced as a result of chemical reaction between titanium and silica by forming Si-O-Ti bonds. In addition the luminescence intensity decreased with increase in titanium content. Ting [5] et al prepared Er$^{3+}$-Yb$^{3+}$ codoped TiO$_2$ films on fused silica by sol-gel process. They studied physical characteristics and infrared fluorescence properties at lower annealing temperature than SiO$_2$ films with Er$^{3+}$-Yb$^{3+}$ codoped, annealed at optimal temperature of 985°C. The microstructure and optical properties of MgO-TiO$_2$ composite thinfilms prepared by radio frequency magnetron sputtering were studied by Ye et al [6] and they observed a broad photo luminescence band in the visible region with high Mg content and was considered resulted from oxygen vacancies. Nagaraju et al [7] investigated the spectroscopic properties like optical absorption, IR, ESR, luminescence and magnetic susceptibility on PbO-As$_2$O$_3$ glasses crystallized with TiO$_2$ and confirmed the presence of Pb$_3$O$_4$, Ti[As$_2$O$_7$], Pb[As$_2$O$_6$], Pb$_3$[AsO$_4$]$_2$, PbTi$_3$O$_7$ and Ti$_2$O$_3$ crystal phases in the glass matrix. Abdel-Baki et al [8] optically characterized the xTiO$_2$-(60-x)SiO$_2$-40Na$_2$O glasses, especially absorption edge, Fermi level, electronic polarizability and optical basicity. Raghavaiah et al [9] studied the spectroscopic properties of titanium ions of various concentrations in PbO-Sb$_2$O$_3$-As$_2$O$_3$ glasses and concluded that glasses with 0.25 mol% of TiO$_2$ are more suitable for the practical applications like non-linear optical devices. Song et al [10] demonstrated the conversion of near-ultraviolet
radiation of 250-350 nm into visible emission of 450-600 nm and NIR emission of 970-1100 nm in the Yb$_2$O$_3$ doped transparent 40SrO-20TiO$_2$-40SiO$_2$ glasses. X ray absorption near edge structure analysis of valence state and coordination geometry of Ti ions in borosilicate glasses were done by Yang et al [11]. From their study they concluded that conclusion that usage of reducing agent during melting process favors the formation of fourfold coordinated Ti$^{4+}$ ions in sodium borosilicate glasses.

4. 3 Results and Discussion:

4. 3. 1 Characterization and Physical parameters:

Figure 1 shows the XRD patterns of 0.5 wt% TiO$_2$ doped (CT$_5$ and ST$_5$) glass samples. The absence of sharp Bragg peaks in the XRD patterns confirmed the amorphous nature and the observed broad humps are due to the short range periodicity
in the prepared samples. Remaining samples also showed the similar behavior. The measured density value of CT\(_0\) glass sample is 4.3006 g/cm\(^3\) and it is increased with the integration of SrO. This is expected due to replacement of a lighter cation by heavier one since the density of a glass is very sensitive to the ionic size and atomic weight. In CaO mixed glasses the density is increased with doping of TiO\(_2\) as given in Table 4.1. The increase in density with TiO\(_2\) doping in CaO mixed glasses is also explained in the similar manner as lighter B\(^{3+}\) is replaced by heavier Ti\(^{4+}\) ions.

**Table 4.1** The density (\(\rho\)), molar volume (\(V_m\)), refractive index (\(\mu\)), Ti\(^{4+}\) ion concentration (\(N_i\)), average boron-boron separation \(\langle d_{B-B}\rangle\) and theoretical optical basicity (\(A_{th}\)) of the glasses 10MO.20Bi\(_2\)O\(_3\).\((70-x)B_2O_3.xTiO_2\) \([R=Ca, Sr]\).

<table>
<thead>
<tr>
<th>Sample</th>
<th>x (wt%)</th>
<th>(\rho) (g/cm(^3)) (±0.0001)</th>
<th>(V_m) (cm(^3)/mole) (±0.0001)</th>
<th>(\mu) (±0.0001)</th>
<th>(N_i) X10(^{21}) (ions/cm(^3)) (±0.0001)</th>
<th>(\langle d_{B-B}\rangle) (nm)</th>
<th>(A_{th})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CT(_0)</td>
<td>0.0</td>
<td>4.3006</td>
<td>34.3054</td>
<td>1.7820</td>
<td>--</td>
<td>0.456</td>
<td>0.4348</td>
</tr>
<tr>
<td>CT(_{05})</td>
<td>0.5</td>
<td>4.4159</td>
<td>33.4201</td>
<td>1.7835</td>
<td>0.0901</td>
<td>0.449</td>
<td>0.4354</td>
</tr>
<tr>
<td>CT(_{10})</td>
<td>1.0</td>
<td>4.4197</td>
<td>33.4020</td>
<td>1.7824</td>
<td>0.1803</td>
<td>0.447</td>
<td>0.4360</td>
</tr>
<tr>
<td>ST(_0)</td>
<td>0.0</td>
<td>4.5752</td>
<td>33.2855</td>
<td>1.7874</td>
<td>--</td>
<td>0.451</td>
<td>0.4374</td>
</tr>
<tr>
<td>ST(_{05})</td>
<td>0.5</td>
<td>4.4954</td>
<td>33.8868</td>
<td>1.7855</td>
<td>0.0888</td>
<td>0.452</td>
<td>0.4379</td>
</tr>
<tr>
<td>ST(_{10})</td>
<td>1.0</td>
<td>4.5825</td>
<td>33.2530</td>
<td>1.7820</td>
<td>0.1811</td>
<td>0.446</td>
<td>0.4386</td>
</tr>
</tbody>
</table>

However, the decrease in density at lower concentration of TiO\(_2\) in SrO mixed glasses is attributed to any one of the following (i) formation of octahedral Ti\(^{4+}\) [0.605 Å] than
tetrahedral Ti$^{4+}$ [0.42 Å] (ii) formation of electron and/or hole centers in the glass network [12]. Among which second one is proved from EPR studies. The increase in density with decrease of molar volume is another indication of more compactness of the glass structure. The molar volume and some important physical parameters are also incorporated in Table 4.1. The average boron-boron separation $\langle d_{B-B} \rangle$ is calculated [13] to get more insight about glass network using the following Eq.

$$\langle d_{B-B} \rangle = \left[ \frac{V_m}{N_A} \right]^{1/3}$$  \hspace{1cm} \text{--- (4.1)}

where $N_A$ is Avogadro’s number, $6.0228 \times 10^{23}$ mol$^{-1}$ and $V_m^B$ is the volume containing one mole of boron atoms with the given glass network as boron is central atom of BO$_{3/2}$ and BO$_ {4/2}$ units, is given by

$$V_m^B = \frac{V_m}{2(1-x_B)}$$  \hspace{1cm} \text{--- (4.2)}

Where $x_B$ refers to the molar fraction of B$_2$O$_3$. The calculated values of the average boron-boron separation are listed in Table 4.1. Generally $V_m^B$ depends on the cations present in the glass network and hence depends on the radius of the alkaline earth ions. With the incorporation of SrO at the expense of CaO leads to a substantial decrease in boron-boron separation though the borate percentage is fixed.

4.3.2 Optical Absorption Studies:

Figure 4.3 (a) and (b) reveal the absorption spectra of the CaBiB:Ti and SrBiB:Ti glasses in the wavelength region 400-1400 nm at room temperature. A small
**Fig 4.3(a) & (b)** Absorption spectra of CaBiBO₄:Ti and SrBiBO₄:Ti glasses respectively.

**Fig 4.4.** Absorption spectra of as prepared glasses for the absorption band around 685 nm.
absorption band around 823 nm along with a feeble band at 685.5 nm is observed in CT₀ glass sample. The former band is attributed to the \( ^3P_0 \) to \( ^3P_2 \) electronic transition of Bi⁺ radicals [14] and according to Zhou et al [15] the later band, which is clearly shown in Fig 4.4, is attributed to the electronic transitions of \( ^2P_{1/2} \) to \( ^2P_{3/2} \) of the Bi²⁺ ions.

Interestingly, by the substitution of CaO with SrO the intensities of above said absorption peaks are observed to diminished. With the doping of TiO₂ in calcium series the peak at 823 nm is quenched along with red shift and a small broad hump of absorption band at 609 nm is noticed. The red shift of the absorption band is clearly due to decrease of energy separation between the \( ^3P_0 \) and \( ^3P_2 \) energy levels (\( ^3P_2 - ^3P_0 \)) which is equal to the amount \( 10Dq \) [16], where \( D = \frac{35Ze^2}{4a^2} \) (where ‘a’ is Bi-O bond length) is a factor that depends on the ligand oxygen ions and \( q = \left( \frac{2}{105} \right) \langle r^4 \rangle \) (where ‘r’ is the radial distance of the electron). Therefore, the red shift of the band is a consequence of either decrease of D (increase of ‘a’) and/or decrease of radial position of electron cloud. The decrease in the intensity of absorption bands around 823 and 685.5 nm by the incorporation of TiO₂ into CT₀ glass may be due to the reaction of Ti⁴⁺ ions with the bismuth radicals. The observed broad nature of the band is due to the existing nuclear configurational instability in the excited state, i.e., by the Jahn-Teller effect [17]. In TiO₂ doped glass matrices, there is a possibility for thermal reduction of Ti⁴⁺ ions to Ti³⁺ at higher temperatures (1050 °C) during melting process. We, therefore, propose that the absorption band observed at 609 nm is due to \( ^2T_{2g} \rightarrow ^2E_g \) transition of octahedral Ti³⁺ ions and in all the doped glasses.
4.3.3 Theoretical optical basicity:

Theoretical optical basicity values of all glasses are calculated [18] using the following relation and are presented in Table 2.

\[ \Lambda_{th} = \sum_{i=1}^{n} \frac{Z_i r_i}{|Z_0| \gamma_i} \]  --- (4.3)

Here ‘n’ is the number of cations present, \( Z_i \) is the oxidation number of the \( i^{th} \) cation, \( r_i \) is the ratio of the number of \( i^{th} \) cation to the number of oxides present and \( \gamma_i \) is the basicity moderating parameter of the \( i^{th} \) cation. Using the following equation the ‘\( \gamma_i \)’ values are calculated.

\[ \gamma_i = 1.36(x_i - 0.26) \]  --- (4.4)

where ‘\( x_i \)’ is Pauling electro negativity of the cation. In the present glasses the gradual replacement of CaO with SrO and doping of TiO\(_2\) have influenced the value of optical basicity, and it is found to increase with the increase of dopant concentration and is explained as below: since, the optical basicity of a chemically complex glass is represented by the mean polarization state of the ligands \([\text{O}^-]\) and their mean ability to transfer fractional charges to the central cation [19], increase in \( \Lambda_{th} \) suggests that an increase of localized donor pressure on cations of glass matrix. In other words, the covalence of the glass network decreases. Besides, optical basicity also changes depending on the role of network formers and modifiers. The network formers interact covalently with oxygen, while the modifiers are the elements that interact ionically. Moreover, Duffy et al [20] concluded that the polarizability of oxygen ions is directly
proportional to the optical basicity. The increase in the polarizability of oxygen ions is another indication of increase of the concentration of NBOs in the glass matrix [21].

4. 3. 4 Emission Studies:

Figure 4.5 (a), (b) and (c), (d) shows emission spectra of all the samples excited with 360 and 514 nm respectively. CT<sub>0</sub> glass exhibits a broad emission band covering entire visible light range, centered at 475 nm with three shoulders at 415, 445 and 513 nm. Lakshminarayana et al [22] also observed the similar visible luminescence results for bismuth containing glass samples. With the integration of Sr<sup>2+</sup> ions the emission is quenched and red shifted to 520 nm. It is well known that by choosing appropriate hosts, the luminescence of Bi<sup>3+</sup> can be varied from ultraviolet, blue to even green. Bordun et al [23] reported that such variation in emission is due to change in point symmetry of Bi<sup>3+</sup> ion from D<sub>2</sub>, C<sub>3i</sub> to C<sub>2</sub> due to electronic transition of 3P<sub>1</sub> to 1S<sub>0</sub>. Additionally the emission intensity and FWHM is increased with 0.5 wt% doping of TiO<sub>2</sub>, in CaO mixed glasses, however, the intensity is decreased at higher concentration of dopant. A reverse trend is observed in strontium series. By the addition of 0.5 wt% of TiO<sub>2</sub> to ST<sub>0</sub> glass the emission is quenched with the same peak position. Further addition of TiO<sub>2</sub>, leads a drastic increase of shoulder peaks at 417, 439 and 460 nm. Moreover, the mechanism for green emission in doped glasses is not clear. It was reported that this visible green emission is also due to the oxygen deficient defects in TiO<sub>5</sub> octahedra [24]. But the presence of similar emission band in Ti<sup>4+</sup> free glass clearly suggests that the green emission is most likely originated from 3P<sub>1</sub> to 1S<sub>0</sub> transition of Bi<sup>3+</sup> ions with C<sub>2</sub> point symmetry, as suggested by Bordun et al [23], yet there is an
indirect relationship with the Ti$^{4+}$ ions. Clearly the introduction of TiO$_2$ greatly enhances the intensity of the green emission and the FWHM in CaO mixed glasses.

**Figure 4.5 (a) and (b) Emission spectra of CaBiBO$_4$:Ti and SrBiBO$_4$:Ti glasses respectively with excitation of 360 nm. (c) and (d) Emission spectra of CaBiBO$_4$:Ti and SrBiBO$_4$:Ti glass samples respectively when excited at 514 nm.**
It indicates that in calcium series, the number of Bi\(^{3+}\) ions is increased but the point symmetry of Bi\(^{3+}\) ions is not changed. Where as in the of SrO mixed glasses the decrease in Bi\(^{3+}\) emission intensity is either due to decrease of Bi\(^{3+}\) ions or non radiative dissipation of excitation energy. According to Bordun et al [23] the splitting and increase of emission bands at 471 nm and 439 nm at the expense of 520 nm emission band is due to increase of Bi\(^{3+}\) ions with C\(_3\)\(_i\) point symmetry at an expense of Bi\(^{3+}\) ions with C\(_2\) point symmetry. In strontium series, based on the above discussion, introduction of TiO\(_2\), Ti\(^{4+}\) ions are expected to react with bismuth radicals as a result Ti\(^{4+}\) ions affect the site symmetry or environment of Bi\(^{3+}\) ions from C\(_2\) to C\(_3\)\(_i\) since the concentration of Bi\(_2\)O\(_3\) is fixed in all present glasses.

The observed red emission, with the excitation at 514 nm, in Fig 4 (c) and (d) has been ascribed to the Bi\(^{2+}\) ions. The detailed mechanism of this luminescence has been investigated [25-27] and such red luminescence arises from the electron transition between the first excited level \(^2\)P\(_{3/2}\) and the ground level \(^2\)P\(_{1/2}\) of Bi\(^{2+}\) ions [15]. The decrease in peak intensity and area, by the integration of SrO, of the emission peak could be ascribed to decrease in the Bi\(^{2+}\) luminescence centers. Murata et al. and Ren et al. [28-30] found that the concentration of the luminescent centers and the luminescence intensity decreased with the increment in the basicity of the glasses.

4.3.5 Electron Paramagnetic Resonance:

Figure 4.6 shows the EPR spectra of all doped glasses at room temperature. From the figure a feeble resonance signal is observed around g=2.06. Interestingly, an
additional EPR signal around $g=2.24$ is observed only in ST$_{05}$ glass sample. Besides optical studies the observed small signal around 2.06 confirms the partial (very less) reduction of Ti$^{4+}$ (3d$^0$) ions in to Ti$^{3+}$ (3d$^1$) ions during the melting process.

Fig 4.6. ESR spectra of R$\beta$BO$_4$:Ti (R=Ca, Sr) glasses at room temperature.
Many researchers [31-32] reported that the Ti$^{3+}$ ions mostly occupy the octahedral environment with different degrees of distortion give g values ranging from 1.925 to 1.99. In the present study, therefore the higher g values around 2.06 indicate the higher degree of distortion in octahedral symmetry of Ti$^{3+}$ ions. Therefore, such higher degree of distortion around Ti$^{3+}$ ions is due to the high polarizing nature of Bi$^{3+}$ ions in the glass matrix. Moreover, the observed small additional EPR signal around 2.24 is attributed to electron centers as follows: by recollecting the data of density, in calcium series the density is gradually increased with TiO$_2$ doping. Where as in SrO mixed glasses the density is found to decrease in ST$_{05}$ glass and there after increased beyond this concentration, which is ascribed to either boron electron centers (BEC) or non bridging oxygen hole centers [12]. Alternatively, the quenching action of emission from ST$_0$ to ST$_{05}$ of the present glasses may also be explained by the considering electron-hole recombination occurs by means of the energy transfer of exciton recombination to the excited states of P band of bismuth ion, this is followed by nonradiative relaxation of the excited ion with phonon emission. This is possible because the free electron (or the hole) does not have sufficient electron–phonon coupling necessary for the self trapping to give rise to radiative recombination; on the other hand, the exciton has a strong coupling with the lattice so that predominant nonradiative recombination occurs with the phonon emission [33].

4.3.6 FTIR:

IR transmission spectra of all present glasses under investigation are given in Figure 4.7(a) & (b). The band positions and their corresponding assignments are presented in
Table 4.2. Broad bands are resulted due to convolution of individual bands with each other. For $CT_0$ glass sample, principle bands are observed at 1469, 902 and 683 cm$^{-1}$ with three shoulders around 1390, 1262 and 1053 cm$^{-1}$. Moreover, one feeble band around 423 cm$^{-1}$ is also noticed. By the integration of SrO the centers of the bands around 1469 and 902 cm$^{-1}$ are blue shifted and that of 1053 cm$^{-1}$ is red shifted. By the gradual replacement of $B_2O_3$ with $TiO_2$, the intensities of the bands correspond to borate structural units are decreased and the band at 680 cm$^{-1}$ is red shifted in both the series. In strontium series a small feeble band around 740 cm$^{-1}$ is noticed in 0.5 wt% $TiO_2$ doped glass matrix and is gradually diminished with further addition of $TiO_2$.

**Fig 4.7.** (a) & (b) IR spectra of $CaBiBO_4$:$Ti$ and $SrBiBO_4$:$Ti$ glasses respectively.

To augment the understanding of structural changes in the present glass network, it is helpful to analyze the obtained results in the light of bismuth borate glasses. It is widely
accepted [34] that incorporation of Bi₂O₃ into B₂O₃ leads to conversion of SP² planar BO₃ units to more stable SP³ tetrahedral BO₄ units and also creates non bridging oxygens. Each BO₄ unit is linked to two other similar units and the structure leads to the formation of long tetrahedron chains. However, addition of alkaline earth ions (RO) into glass network transfers the BO₄ tetrahedral into BO3, by forming a ROₙ polyhedron when it is surrounded by several BO₄ tetrahedrons. This structure behaves like a defect in the bismuth borate network. In the present investigation the observed broad bands in the regions from 1500 – 1100 cm⁻¹ and from 1100 – 800 cm⁻¹ are assigned to the stretching vibrations of both triangular BO₃ and tetrahedral BO₄ units respectively. The band at 683 cm⁻¹ is attributed to B-O-B bending vibration. Whenever small amount of dopant is added to both the series the band corresponds to B-O⁻ stretch in BO₂O⁻ units is increased. Besides, at higher concentration of TiO₂ the red shift of the band around 902 and 935 cm⁻¹ in calcium and strontium series respectively can be explained by taking into the account increase of the band at 423 cm⁻¹ which is attributed to either formation or increase of BiO₆ units. In both the series, the red shift of B-O-B bending band, with TiO₂ doping can be explained by the formation of a new bridging bond of B-O-Ti, which is formed by the degeneracy of B-O-B bending vibration with TiO₆ units [3]. As stretching force constant of Ti-O bond is less than that of B-O bond, the effective force constant of B-O-Ti bond decreased. An additional band at 740 cm⁻¹ for ST₀₅ sample is due to Ti-O-Ti symmetric stretching vibrations of TiO₄ units and is gradually disappeared at higher concentration of TiO₂. The gradual disappearance of Ti-O-Ti symmetric stretching bond at 1.0 wt% concentration of TiO₂
Table 4.2 Assignment of absorption bands in the infrared spectra (with a probable error of ±0.1 cm\(^{-1}\)) of the glasses

10RO.20Bi\(_2\)O\(_3\).(70-x)B\(_2\)O\(_3\).xTiO\(_2\) [R=Ca, Sr].

<table>
<thead>
<tr>
<th>CT(_0)</th>
<th>CT(_{05})</th>
<th>CT(_{10})</th>
<th>ST(_0)</th>
<th>ST(_{05})</th>
<th>ST(_{10})</th>
<th>Assignment</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>423</td>
<td>424</td>
<td>433</td>
<td>422</td>
<td>423</td>
<td>430</td>
<td>Vibrations of Bi-O bonds of different lengths in the distorted BiO(_6) octahedral units</td>
<td>[18, 35]</td>
</tr>
<tr>
<td>683</td>
<td>682</td>
<td>668</td>
<td>682</td>
<td>686</td>
<td>677</td>
<td>B-O-B bend</td>
<td>[18, 36, 37]</td>
</tr>
<tr>
<td>902</td>
<td>879</td>
<td>864</td>
<td>935</td>
<td>918</td>
<td>867</td>
<td>B-O stretch in BO(_4) units from diborate groups and/or stretching vibrations of Bi-O bonds in BiO(_6) units</td>
<td>[18, 35, 36, 37]</td>
</tr>
<tr>
<td>1053</td>
<td>1065</td>
<td>1062</td>
<td>1048</td>
<td>1049</td>
<td>1081</td>
<td>Stretching vibrations of B-O bonds in BO(_4) units from tri, tetra and penta borate groups.</td>
<td>[18, 36, 37]</td>
</tr>
<tr>
<td>1262</td>
<td>1263</td>
<td>1263</td>
<td>1242</td>
<td>1247</td>
<td>1255</td>
<td>B-O sym stretch in BO(_3) units from pyro and ortho borate groups</td>
<td>[18, 36, 37]</td>
</tr>
<tr>
<td>1390</td>
<td>1392</td>
<td>1385</td>
<td>1384</td>
<td>1388</td>
<td>--</td>
<td>B-O sym stretch in BO(_3) units from varied types of borate groups</td>
<td>[18, 36, 37]</td>
</tr>
<tr>
<td>1469</td>
<td>1474</td>
<td>1493</td>
<td>1481</td>
<td>1472</td>
<td>1494</td>
<td>B-O(^-) stretch in BO(_2)O(^-) units from varied types of borate groups</td>
<td>[18, 36, 37]</td>
</tr>
</tbody>
</table>

References:
[18, 35, 36, 37]
is explained by considering its higher density and lower molar volume than ST\(_0\) and ST\(_{0.5}\). In other words the compactness of the ST\(_{1.0}\) glass samples is increased which may due to filling of titanium ions in the interstices of the bismuth borate network indicating the formation of B-O-Ti and Bi-O-Ti linkages by decreasing B-O-B as well as Ti-O-Ti bonds hence, decreases the intensities of 682 and 740 cm\(^{-1}\) bands respectively. The absence of the band at 740 cm\(^{-1}\) in calcium series could also be explained in the above similar manner due to formation of cross linked bonds in the glass network.

**References:**


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