Physical and optical investigations of Bi$_2$O$_3$-TeO$_2$-B$_2$O$_3$-GeO$_2$ glasses

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Abstract

A new series of quaternary glasses with chemical composition $x$Bi$_2$O$_3$•(80-x)TeO$_2$•10B$_2$O$_3$•10GeO$_2$ where 40 ≤ $x$ ≤ 65 have been prepared by melt quenching technique. X-ray diffraction measurements have been achieved to check the amorphous nature of the glasses. The effect of Bi$_2$O$_3$ content on the physical, thermal and optical properties of the prepared glasses was studied. It is observed that oxygen packing density decreased with the increase of molar volume with increasing Bi$_2$O$_3$ content implying the formation of non-bridging oxygen’s and expands the glass. The glass transition temperature ($T_g$) increased whereas the glass stability decreased with Bi$_2$O$_3$. In addition to that, indirect optical band gap and Urbach energy values of the titled glasses have been calculated from Tauc plots using absorption spectra. The indirect optical band gap (E$_{opt}$) decreased with the increase of Bi$_2$O$_3$ concentration in the present glass system. The Raman spectroscopy at room temperature was employed to study the influence of bismuth oxide on the boron-oxygen network structure. The analysis of Raman spectra shows the presence of fundamental vibrations of TeO$_3$, GeO$_6$, BO$_3$, BO$_4$, BiO$_6$ structural units.

1. Introduction

Glasses that are prepared from tellurium oxide have been gaining much interest owing to their scientific and technical advantages. Low phonon-energy and the large third order non-linear susceptibility make these glasses as important counterparts in optical amplifiers. Since TeO$_2$ is a conditional glass former, one cannot prepare glass from it under normal quenching rates. Adding other oxides like B$_2$O$_3$ to TeO$_2$ results in the successful formation of TeO$_2$ based glasses.

Borate and boro-tellurite glasses have been widely studied due to their unique physical, optical and mechanical properties. The important applications of boro-tellurite glasses include, fiber optical communication systems, non-linear optical devices and lasers [1–3]. High transparency, low melting temperature, and stability against devitrification are the main characteristics of these glasses. The binary B$_2$O$_3$-TeO$_2$ glass network system contained the structural units of TeO$_4$, BO$_3$, and B$_2$O$_6$ [4].

Ayuni et al [5] reported a decrease in the indirect optical band gap energy and the band tailing of TeO$_2$-B$_2$O$_3$-ZnO glass system and an increase in the refractive index as TeO$_2$ content decreases. And this change is attributed to the creation of non-bridging oxygens and these non-bridging oxygens increases with decrease in TeO$_2$. Elkhoshkhany et al [6] observed that the glass transition temperature and crystallization temperature of Li$_2$O-B$_2$O$_3$-TeO$_2$ glass system increased as a function of B$_2$O$_3$ whereas the optical energy gap and Urbach energy decreased and is attributed to the increase of the degree of disorder of the glass network. Usman et al [7] prepared Ho$^{3+}$ ion doped zinc boro-tellurite glasses and studied FTIR. They found that the increase of B$_2$O$_3$ content in the system can transform TeO$_3$ into TeO$_2$ as well as BO$_3$ into BO$_4$ structural units. As a result of this the bridging
oxygen vacancies, refractive index, density, and oxygen packing density increased while the optical band gap and molar volume showed a decreasing trend.

Since Bi$_2$O$_3$ and TeO$_2$ are glass formers, the addition of heavy metal oxides such as Bi$_2$O$_3$, WO$_3$ or PbO to boro-tellurite glasses can change the structure of the glass. Bismuth is one of the heavy metals considered to be harmless, non-toxic and non-carcinogenic material has electronic applications, ceramic production and also used in high temperature superconductors because of the high polarizability of Bi$^{3+}$ cations [8–12]. Addition of heavy metal oxides like Bi$_2$O$_3$ to tellurium glasses modifies physical as well as optical properties of the system. TeO$_2$-Bi$_2$O$_3$ glasses exhibit high second and third order non-linear optical susceptibility due to which they are used in up-conversion lasers and non-linear optical materials. There are many reports on the structural studies of the binary glasses such as B$_2$O$_3$-Bi$_2$O$_3$, B$_2$O$_3$-GeO$_2$ [13, 14]. Hasegawa [15] and Saddeek et al. [16] developed Bi$_2$O$_3$-TeO$_2$-B$_2$O$_3$ ternary glass system and investigated their physical, linear and non-linear optical properties. Munoz-Martin et al. [17] prepared ternary tellurite-tungstate glass system with alkaline oxide, ZnO, Bi$_2$O$_3$ or Li$_2$O as third component and demonstrated that these ternary glasses are promising materials for developing broadband integrated optical amplifiers. Zhou et al. [18] prepared and characterized new tellurium quaternary TeO$_2$-PbO-Bi$_2$O$_3$-B$_2$O$_3$ glass system and explained the variations in thermal stability with the glass composition using FTIR measurements. The present glasses can be used for photonic devices and low melting point sealing glasses.

GeO$_2$ is a typical glass former that consists of tetrahedral and octahedral germanium coordinated by oxygen. Bismuth germanate glasses have been widely used various applications such as infrared transmitting windows, as active media for Raman optical media, and thermal and mechanical sensors [19–21]. Mansour [22] prepared Li$_2$O-B$_2$O$_3$-GeO$_2$ glasses with high Li$_2$O content and measured Molar volume, density, and Raman spectra of the prepared glasses. Glasses containing Bi$_2$O$_3$ in combination of GeO$_2$ have been investigated as IR transmitting windows and optical fibers with low loss [23]. Fan et al. [24] performed thermal, infrared, Raman and XPS spectroscopic studies on prepared Bi$_2$O$_3$-B$_2$O$_3$-GeO$_2$ ternary glass system. Xia and Yang [25] carried out thermal, emission and absorption measurements on Bi$_2$O$_3$-GeO$_2$-WO$_3$ and Bi$_2$O$_3$-GeO$_2$-BaO glasses and concluded that Bi$^{5+}$ ions are responsible for broad band emission. There are many reports on GeO$_2$ ternary glasses such as GeO$_2$-PbO-Nb$_2$O$_5$, GeO$_2$-PbO-CaCO$_3$ and Li$_2$O-GeO$_2$-P$_2$O$_5$ [26–28].

In order to exploit the technological potential of glasses, it is crucial to investigate the structural studies by infrared and Raman spectroscopy. These two methods play an important role in the identification of the basic structural units like BO$_4$, BO$_5$, TeO$_4$, TeO$_6$. Structural investigations of Bi$_2$O$_3$, Bi$_2$O$_3$, TeO$_2$ and GeO$_2$ based glasses were published [29, 30]. Osaka et al [31] and Mattarelli et al. [32] examined the structure of GeO$_2$-TeO$_2$ by EXAFS and Raman studies. Osipov et al. [33] employed Raman and FTIR spectroscopy to study the influence of zinc oxide on BaO-B$_2$O$_3$ glass matrix. Vani et al. [34] presented the Raman data on fluorotellurite glasses based on zinc and barium fluorides and observed the formation of more non-bridging fluorine instead of non-bridging oxygens. Quaternary glasses Bi$_2$O$_3$-TeO$_2$-B$_2$O$_3$-TiO$_2$ were investigated by Raman studies [1] and found that the coordination number of tellurium ions with oxygen remains constant with varying TiO$_2$ content. Recently Seema Thakur et al. [35] investigated the structure of B$_2$O$_3$-Bi$_2$O$_3$-NiO glasses and revealed that glass network comprises of BiO$_3$, BiO$_6$ BO$_3$ and BO$_4$ units.

To the best of our knowledge, there are no proper reports on Bi$_2$O$_3$-TeO$_2$-B$_2$O$_3$ glasses containing GeO$_2$. We have studied the effect of Bi$_2$O$_3$ content on physical, thermal, optical and structural properties of Bi$_2$O$_3$-TeO$_2$-B$_2$O$_3$-GeO$_2$ glass system. Further, the present study optimizes the content of Bi$_2$O$_3$ in Bi$_2$O$_3$-TeO$_2$-B$_2$O$_3$-GeO$_2$ glass system to use it as non-linear optical material in different types of technological applications.

2. Materials and methods

2.1. Materials

High purity bismuth oxide (Bi$_2$O$_3$), tellurium oxide (TeO$_2$), germanium oxide (GeO$_2$) and boron trioxide (B$_2$O$_3$) (Sigma Aldrich 99.999% pure) were used as starting materials.

2.2. Glass preparation

The present glass samples of compositions xBi$_2$O$_3$-(80-x)TeO$_2$-10B$_2$O$_3$-10GeO$_2$ (x = 40, 45, 50, 55, 60 and 65 mole %) were prepared using conventional quenching method. A detailed procedure followed for the synthesis of xBi$_2$O$_3$-(80-x)TeO$_2$-10B$_2$O$_3$-10GeO$_2$ (x = 40, 45, 50, 55, 60 and 65 mole %) has been given in electronic supplementary material (ESM) is available online at stacks.iop.org/MRX/6/125209/mmedia.
2.3. Characterization

Structural characterization of the glass samples was done by using x-ray diffraction technique. Differential scanning calorimetry was used for the thermal characterization of the samples. Physical properties of the glasses like, density, density related parameters such as molar volume, oxygen packing density, oxygen molar volume, bismuth ion concentration, polaron radius, and inter-nuclear distance were systematically examined. Optical properties of the glasses were investigated using UV-Visible spectroscopy. The investigated optical parameters are cut-off wavelength, indirect optical band gap energy, Urbach energy $\Delta E$, Possion’s ratio (Makishima and Mackenzie) $\mu_{\text{cal}}$, Possion’s ratio (Bridge) $\mu'_{\text{cal}}$, bond density and average coordination number. The working conditions of the characterization tools along with the procedures followed for the investigation of structural, thermal, physical, and optical properties have been given in ESM.

3. Results and discussions

3.1. Structural analysis

Figure 1 shows the XRD patterns obtained for $x\text{Bi}_2\text{O}_3-(80-x)\text{TeO}_2-10\text{B}_2\text{O}_3-10\text{GeO}_2$ glass system. As observed from the figure, the broad low intense peak appeared at the angles $2\theta$°–30° confirms the amorphous nature of the sample without any strong and high intense peaks.

3.2. Physical properties

The experimental density of the present glasses with composition $x\text{Bi}_2\text{O}_3-(80-x)\text{TeO}_2-10\text{B}_2\text{O}_3-10\text{GeO}_2$ is presented in figure 2 with varying Bi$_2$O$_3$ content. It is revealed that the density of the present glasses varied nonlinearly with the increase of Bi$_2$O$_3$ content, the maximum value obtained for $x = 50$ mole% of glass.

Theoretically, glass density from its chemical composition is given by the following equation [36].

$$\rho_{th} = 0.53 \frac{\sum (M_i x_i)}{\sum (V_i x_i)}$$  \hspace{1cm} (1)

where $M_i$ is the molecular weight (Kg mole$^{-1}$), $x_i$ is the mole fraction (mole%), and $V_i$ is the packing density parameter (m$^3$ mole$^{-1}$). The packing density parameter $V_i$ for $M_i\text{O}_y$ can be calculated using the following formula

$$V_i = \frac{4}{3} \pi N_a (x_i r_M^3 + y_i r_O^3)$$  \hspace{1cm} (2)

where $r_M$ and $r_O$ are the ionic radii of metal and oxygen respectively. Shannon’s ionic radii were used [37, 38] for the present study. The packing density parameter $V_i$ (m$^3$ mole$^{-1}$) of various metal oxides used in the present study are $26.1 \times 10^{-6}$ (Bi$_2$O$_3$), $14.7 \times 10^{-6}$ (TeO$_2$), $20.8 \times 10^{-6}$ (B$_2$O$_3$) and $14.0 \times 10^{-6}$ (GeO$_2$). The theoretical density and the experimental density values of the presented glasses were summarized in table 1. The molar volume ($V_m$), values increase from 50.09–65.94 cc mole$^{-1}$ with Bi$_2$O$_3$ content (from 40 to 65 mole%).
This implies that the number of non-bridging oxygen atoms increases and the glass becomes loosely packed. Oxygen packing density (OPD) varies from 49.91 - 41.704 g-atm/cc as Bi₂O₃ content increases. Oxygen molar volume ($V_o$) values vary from 20.036 - 23.978 cc mole$^{-1}$ with Bi₂O₃ content. Graphical representation of the above results is given in figure 3, where the decreasing of OPD and increasing of $V_o$ with increasing Bi₂O₃ content can be visualized. The typical behavior of the sample indicates that the network structure of the present glass is more open and becomes loosely packed.

Other physical parameters such as Bi³⁺ ion concentration ($N$), polaron radius ($r_p$), and inter-nuclear distance ($r_i$) were also calculated and can be seen in table 1. Decreasing trend of $r_p$ and $r_i$ and increase of Bi³⁺ concentration with increasing Bi₂O₃ content were observed. The $r_p$ of each prepared glass is observed less than the corresponding Bi-Bi spacing.

### 3.3. Differential scanning calorimetry

Figure 4 presents the DSC thermograms for the prepared glasses with different Bi₂O₃ content. A typical DSC thermogram for 40Bi₂O₃-40TeO₂-10B₂O₃-10GeO₂ glass is shown in figure 4 (inset). A single endothermic peak at 455 °C corresponds to the glass transition temperature ($T_g$), followed by the onset of crystallization temperature ($T_x$). The exothermic peak at 569 °C is assigned to the full crystallization temperature ($T_c$).

Furthermore, the good homogeneity of the glasses also revealed from the single peak in $T_g$. The thermo-dynamical parameters such as $T_g$ and $T_x$ were determined and represented in table 2. The $T_g$ values increase from 455 °C to 540 °C with increase of Bi₂O₃ content. Generally, the thermal stability of the glass can be estimated from the difference between the $T_x$ and $T_g$ (i.e., $S = T_x - T_g$). The thermal stability for the prepared glasses was calculated and tabulated in table 2. The wide thermal stability range is highly favorable for the process of glass formation. Figure 5 plots the variation of $T_g$ as a function of Bi₂O₃ content.

It was found that the glasses with $S > 100$ are suitable for drawing optical fibers. The observed $S$ values of the prepared glasses decrease with the increase of Bi₂O₃ content. Structural changes presented in the glass
network may help in the explanation of the thermal characteristic variations. The addition of octahedrally coordinated bismuth atoms assists the formation of mixed bonds Te-O-Bi and B-O-Bi which are highly imperishable and modifies the glass network. Saddeek et al.\cite{42} reported that the increase of Bi$_2$O$_3$ in B$_2$O$_3$-TeO$_2$-Bi$_2$O$_3$ glass system increases the packing density and rigidity of the network. Elkhoshkhany et al.\cite{43} reported that the $T_g$ is a function of the stretching force constant and the average crosslink density. In the present glass system, the values of the average coordination number ($m$) increase from 4.8 to 5.3 (table 2). The increasing average coordination number of the glass network increases the rigidity and leads to an increase in the $T_g$.

The cross link density ($\pi_c$) of the glasses was calculated by the following equation\cite{44}

$$\pi_c = \frac{\sum x_i (n_c)_i (N_c)_i}{\sum x_i (N_c)_i}$$  \hspace{1cm} (3)

where $x_i$ is the molar fraction of each component $i$, $N_c$ is the number of cations per glass formula unit, $n_c = n_i - 2$, $n_i$ is the coordination number of cations (6 for Bi$_2$O$_3$ and 4 for TeO$_2$, B$_2$O$_3$, and GeO$_2$)\cite{45}. The calculated values of the crosslink density increases from 3.06 to 3.48 as Bi$_2$O$_3$ content is increased from 40 to 65 mol% (table 2). In addition to the coordination number, the $T_g$ increases also with the cross link density. Poisson’s ratio depends on the crosslink density. High crosslink density glasses possess Poisson’s ratio of above 0.1–0.2 and for low crosslink density glasses, the Poisson’s ratio ranges from 0.3–0.5. Theoretically, Poisson’s ratio
The ratio of the glasses was calculated by Makishima and Mackenzie theory [46],
\[ \mu_{\text{cal}} = 0.5 - \frac{1}{7.2 V_i} \]  
and by using the theory of Bridge \( (\mu'_{\text{cal}}) \) [47],
\[ \mu'_{\text{cal}} = 0.28 (\Pi)^{-0.25} \]  
The total packing density \( V_t \) was calculated using the equation
\[ V_t = \left( \frac{1}{V_m} \right) \sum V_i x_i \]  
where \( V_i \) is the packing density factor of the oxides was defined in equation (10).

Poisson’s ratio calculated according to the theory of Makishima & Mekhanzie, and Bridge varies from 0.095 to 0.155, and 0.205 to 0.211, respectively (table 2). This indicates that the present glass samples have high crosslink density. Few structural changes may arise when Bi\(_2\)O\(_3\) replaces TeO\(_2\).

The bond density \( n_b \) which is defined as the number of bonds per unit volume was determined by using the formula [45]
where \( m \) is the coordination number of the glass. In the present glass system the bond density decreases from \( 5.77 \times 10^{22} \) to \( 4.84 \times 10^{22}/\text{cc} \) as the bismuth content is increased from 40 to 65 mole\% (table 2).

### 3.4. Optical properties

The information related to the optically induced transitions, energy gap, and band structure of amorphous glassy materials can be obtained from the optical absorption studies (in particular, absorption edge). A systematic analysis of absorption spectra at lower and higher energies will give the accurate information about the atomic vibrations and electronic states in the atom respectively [48]. The interaction between an electromagnetic wave and a valence electron results in both direct and indirect optical transitions across the energy gap. Figure 6 is the variation of optical absorption intensity with wavelength for the present glasses with composition \( \text{xBi}_2\text{O}_3-(80-\text{x})\text{TeO}_2-10\text{B}_2\text{O}_3-10\text{GeO}_2 \) (\( x = 40, 45, 50, 55, 60 \) and 65 mole\%). The absence of the sharp absorption edge in the figure indicates the glassy state of the sample. The cut-off wavelengths (\( \lambda_c \)) obtained are presented in table 2. Generally, oxygen bond strength and absorption edge are interrelated, change in oxygen bonding alters the absorption edge.

The following equation was used for the determination of the optical absorption co-efficient \( \alpha(\nu) \) at the fundamental absorption edge

\[
\alpha(\nu) = \left( \frac{1}{d} \right) \log \left( \frac{I_0}{I_t} \right)
\]

(8)

Here \( I_0 \) as well as \( I_t \) are the strengths of incident and transmitted rays respectively. Here \( d \) is the thickness of glass sample. The element \( \log (I_0/I_t) \) accord with absorbance. The optical absorption near the edge is strongly dependent on the electronic structure and in amorphous or glassy materials, the band tail arising from the randomness of the bonding. The optical absorption processes depend on the nature of transitions (i.e., direct or indirect or forbidden or permitted), the index \( n \) in the equation for optical absorption coefficient given by the equation [49, 50]

\[
\alpha(\nu) = \left( \frac{B(\nu) - E_{\text{opt}})^n}{h} \right)
\]

(9)

Here \( h\nu \) is the energy of incident photon, \( B \) is a constant related to the amount of band tailing, \( E_{\text{opt}} \) is the optical energy gap and \( n \) is a digit which symbolizes the transition progression (for \( n = 1/2, 2, 3/2, \) and 3 the transitions are direct allowed, indirect allowed, direct forbidden, and indirect forbidden respectively). Figure 7 represents Tauc plots for \( \text{xBi}_2\text{O}_3-(80-\text{x})\text{TeO}_2-10\text{B}_2\text{O}_3-10\text{GeO}_2 \) (\( x = 40, 45, 50, 55, 60 \) and 65 mole\%) glasses. The band gap energies have been calculated by extrapolating linear region of the tauc plots to meet (\( h\nu \)) axis for the indirect allowed transitions (i.e., where \( \alpha(\nu)1/2 = 0 \)). Optical band gap energy (\( E_{\text{opt}} \)) values calculated for all the glasses are given in table 2. The recorded decrease in \( E_{\text{opt}} \) from 3.07 to 2.81 eV is due to the structural changes occurred...
in the prepared glasses. The cation polarizability of the Bi$^{3+}$ ion (1.508 Å$^3$) is weaker as compared to the cation polarizability of Te$^{2+}$ ion (1.595 Å$^3$) which leads to the weakening of bond strengths between metal and oxygen and finally forms the non-bridging oxygen atoms.

Defect concentration in the glass networks was calculated using Urbach energy $\Delta E$. The relation between $\alpha$ ($\nu$) and $\Delta E$ is given by well-known Urbach law [51].

$$\alpha(\nu) = B \exp\left(\frac{h\nu}{\Delta E}\right)$$

(10)

where $B$ is constant and $\Delta E$ is Urbach energy.

The relation can also be written as

$$\ln \alpha(\nu) = \frac{h\nu}{\Delta E} + \text{constant}$$

(11)

Urbach plots (a graph between ln($\alpha$) versus $h\nu$) for all the prepared glasses are shown in figure 8. The values of Urbach energy ($\Delta E$) were determined from the inverse slope of linear regions of Urbach plots and are presented in table 2. Earlier reports [49] suggested that the $\Delta E$ values for amorphous materials should lie between 0.045 and 0.66 eV. Generally, large values of $\Delta E$ convert the weak bond into defects and reduce the long
range order of the material. $\Delta E$ values obtained for the present glass samples are in the range $0.025 - 0.162$ eV which indicates the amorphous nature of the samples. Furthermore, smaller values of $\Delta E$ correspond to the greater stability of the glass network [52]. The values of $\Delta E$ for the present glass samples increase with increase in Bi$_2$O$_3$ content and leads to the decrease in the structural stability which finally results in the increase of defect concentration as well as delocalization of the electrons.

3.5. Raman studies

The room temperature Raman spectra of the glass samples with composition xBi$_2$O$_3$-(80-x)TeO$_2$-10B$_2$O$_3$-10GeO$_2$ in the spectral wavenumber range 120–2500 cm$^{-1}$ are shown figure 9. The obtained spectra were broad in nature having hidden peaks inside it. For better identification of these peaks, Raman spectra is deconvoluted and typical deconvoluted spectra of 40Bi$_2$O$_3$-40TeO$_2$-10B$_2$O$_3$-10GeO$_2$ glass are shown figures 10(a) and (b), respectively. The peak positions of the deconvoluted Raman spectra are presented in table 3.

The Raman spectra of $\alpha$-TeO$_2$ consists of several peaks in the low frequency range. In all the present glasses the Raman strong peaks observed at lower wavenumbers in the range 128–145 cm$^{-1}$ are due to the librational
modes of TeO$_4$ units [1, 53]. The Raman peaks appearing at the positions ranging from 319–335 cm$^{-1}$ can be considered as the vibrational modes of Bi-O-Bi band of the Bi$_{60}$ octahedral structural units. The intensity and area of this band was found to increase with the increase in Bi$_2$O$_3$ content [35, 34].

The Raman band centered at 411 cm$^{-1}$ arises from the symmetric stretching of Ge-O-Ge linkages in GeO$_4$. Jain et al [55] observed this band at 418 cm$^{-1}$ in Rb$_2$O-GeO$_2$ glass system. A well distinguished Raman peak between 529–547 cm$^{-1}$ belongs to Bi-O stretching vibrations (vibrations of bismuth associated with non-bridging oxygens) of Bi$_6$O$_{10}$ octahedral units.

Table 3. Peak positions (cm$^{-1}$) of deconvoluted peaks of Raman spectra with composition of xBi$_2$O$_3$-(80-x)TeO$_2$-10B$_2$O$_3$-10GeO$_2$ glass system for different values of x.

| $X$ | X = 40 | X = 45 | X = 50 | X = 55 | X = 60 | $X = 65$ |
|-----|--------|--------|--------|--------|--------|--------|
| Peak Center | Center (C) | Center (C) | Center (C) | Center (C) | Center (C) | Center (C) |
| 145 | 135 | 130 | 129 | 128 | 128 |
| 319 | 335 | 333 | 324 | 332 | 335 |
| 392 | 411 | 411 | — | 410 | 408 |
| 529 | — | — | 547 | — | 537 |
| 627 | 654 | — | — | 687 | 694 |
| 740 | 739 | 707 | 728 | 701 | 701 |
| 1201 | 1205 | 1202 | 1201 | 1215 | 1210 |
| 1349 | 1351 | 1352 | 1353 | 1353 | 1354 |
| 1471 | 1465 | 1417 | 1477 | 1479 | 1481 |
| 1676 | 1678 | 1681 | 1682 | 1681 | 1684 |
| 1787 | 1774 | 1786 | 1794 | 1768 | 1778 |

The Raman bands observed in the range 1201–1215 cm$^{-1}$ may be assigned to B-O stretching vibrations in BO$_3$ units from boroxol rings [62, 63]. The Raman assignments for all the peaks in the Raman spectra are given in table 4.

| Raman peak position (cm$^{-1}$) | Raman assignments |
|-------------------------------|------------------|
| 128–145 | librational modes of TeO$_4$ units |
| 319–335 | Vibrational modes of Bi-O-Bi band of the Bi$_{60}$ octahedral structural units. |
| 411 | Symmetric stretching of Ge-O-Ge linkages in GeO$_4$. |
| 529–547 | Bi-O stretching vibrations (vibrations of bismuth associated with non-bridging oxygens) of Bi$_6$O$_{10}$ octahedral units |
| 627–654 | Symmetric stretching vibration of Ge-O-Ge linkages in GeO$_4$ Octahedral units |
| 701–740 | Stretching vibrations of Te-O$^-$ bonds (O$^-$ stands for non-bridging oxygens) in TeO$_3$ structural units |
| 1201–1215 | B-O stretching vibrations in BO$_3$ units from boroxol rings |
| 1349–1354 | B-O$^-$ vibrations of the units attached to large segments of the borate networks |
| 1465–1794 | B-O stretching vibrations in BO$_3$ triangular units from varied types of borate groups |

In the present Raman spectra the peak around 701–740 cm$^{-1}$ is related to the stretching vibrations of Te-O$^-$ bonds (O$^-$ stands for non-bridging oxygens) in TeO$_3$ structural units. It is observed that the TeO$_3$ structural groups remains constant throughout the glass system [39]. This Raman peak was observed at 750–760 cm$^{-1}$ in zinc bismuth boro-tellurite glasses [60]. The sharp Raman bands in the present study occurring in the spectral range 1349–1354 cm$^{-1}$ may be assigned to B-O$^-$ vibrations of the units attached to large segments of the borate networks [61]. This band intensity and area remains constant.

The Raman peak intensity observed in the range 1201–1215 cm$^{-1}$ is found to increase with Bi$_2$O$_3$ content. Prominent Raman bands were observed from 1465–1794 cm$^{-1}$ range. These band intensity and area remains constant. The Raman bands observed in the range 1201–1215 cm$^{-1}$ and 1465–1794 cm$^{-1}$ can be assigned to the B-O stretching vibrations in BO$_3$ units from boroxol rings [62, 63].

4. Conclusions

Synthesis of six glass samples with the composition xBi$_2$O$_3$-(80-x)TeO$_2$-10B$_2$O$_3$-10GeO$_2$ where 40 $\leq$ x $\leq$ 65 mol% has been done successfully using melt quenching technique. XRD, density, and UV-Visible characterization of the glass samples were studied. The amorphous nature of the present bismuth tellurium boro
germanate glasses has been confirmed by XRD spectra. The density of the glasses was measured and density related parameters were calculated. It is observed that the molar volume and oxygen molar volume increase with increase in Bi2O3 content, whereas oxygen packing density decreases. Theoretically, Poisson’s ratio of the present glasses calculated by Makishima & Mekhanzie theory and Bridge model was found to vary from 0.095 to 0.155 and 0.205 to 0.211 respectively.

The glass transition temperature is found to increase with increase in Bi2O3 content and the reverse trend is followed by the glass stability. The indirect optical band gap energy for all the glass samples was determined from the Tauc plots, the values were in the range 3.07–2.81 eV. One can conclude that the Bi2O3–TeO2–B2O3–GeO2 glasses in the present work could be considered as candidates suitable for drawing optical fibers. The structure of the present glasses was studied by Raman spectroscopy. The Raman spectra were deconvoluted. The structural result analysis indicates the existence of TeO4, BiO6, BO3, GeO4 units stretching vibrations.

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