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Effect of B$_2$O$_3$ addition on thermal and optical properties of TeO$_2$–ZnO–Bi$_2$O$_3$–TiO$_2$ glasses

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Abstract
New tellurite glasses with composition (in mol%): 60TeO$_2$–(30–x)ZnO–5Bi$_2$O$_3$–5TiO$_2$–xB$_2$O$_3$ (where x = 0, 2.5, 5.0, 7.5 and 10.0) were fabricated using conventional melt quenching method. Compositional dependence of the glasses on their density, thermal, refractive index and optical properties were investigated. X-Ray Diffraction analysis was carried out to confirm the nature of the thus formed glasses. Density, refractive index, and absorption spectra were measured at room temperature from which other glass characteristics such as polaron radius, oxygen packing density, field strength, B$^{3+}$ interatomic distance, band gap energy, and Urbach tail were determined. Thermal characterisation to determine the change in glass transition temperature, glass crystallisation, melting point, and glass stability was carried out using Differential Scanning Calorimetry. A discussion was made in order to understand the results in terms of the ratio of bridging oxygen to non-bridging oxygen ions (BO/NBO). It was found that the addition of B$_2$O$_3$ results in increasing oxygen packing density, glass transition temperature, BO/NBO ratio and band gap energy, while decreasing density, refractive index, field strength, glass stability and Urbach tail energy. With increasing B$_2$O$_3$ concentration density changed from 5.879 to 5.646 g cm$^{-3}$, refractive index 1.875 to 1.741, working temperature range ($\Delta T = 66$ °C) and phonon energy within the range of 736–740 cm$^{-1}$.

1. Introduction
In the last few decades, tellurite glasses have been studied mainly because of their excellent properties in terms of high refractive index, wide transmission window, a high solubility of rare-earth ions, broad range absorption in the infrared region, low phonon energy, low melting point and stability against crystallisation [1, 2]. Making use of these properties, various compositions of tellurite glasses have been extensively researched for broad applications such as optical amplifiers, optical fibre, laser, sensors, ultrafast optical switches, and gamma radiation shielding [3, 4].

To be a good glass matrix used for efficient fibre laser, several important glass features are needed. Two of them are stability against crystallization and low phonon energy. Tellurite glasses are researched partly to seek the right glass composition possessing low phonon energy and high thermal stability. It has been reported that TeO$_2$–ZnO system shows good glass forming ability [5] and therefore has been used as a based glass and developed for various applications [6–10]. However, it was reported that TeO$_2$–ZnO system also shows low thermal stability [8–10]. For this reason, we have developed new glasses by adding Bi$_2$O$_3$, B$_2$O$_3$ and TiO$_2$ into TeO$_2$–ZnO system with expectation to have glasses having properties suitable for fibre laser. Generally, ZnO is added into a glass structure because of dual role it might play. As a network former, Zn$^{2+}$ ions come into the network in the form of ZnO$_4$ structural unit, while as network modifier, these ions are present in octahedral coordination similar to other conventional alkali oxides [11, 12]. Yao et al. [13] reported that addition of ZnO into borate glasses improve the network structure. It is known that B$_2$O$_3$ is a good glass former. It can form a glass by itself. It has been shown that incorporating B$_2$O$_3$ into tellurite glass changes the glass structural unit from TeO$_4$ into TeO$_3$ and TeO$_2$, as well as improving the glass forming ability, transparency, hardness, and rare-
earth ions solubility [14–16]. Incorporating B$_2$O$_3$ into tellurite glass improves glass stability against crystallisation [14–16]. It was reported that incorporation of Bi$_2$O$_3$ into a glass can decrease phonon energy and therefore improve fluorescent efficiency [17, 18].

The objective of this work is to develop novel boro-tellurite glasses as a potential host for rare earth ions used in fibre laser and optical amplifiers. These new glasses were studied in term of the effect of B$_2$O$_3$ addition to partially substitute ZnO on their physical, structural, thermal and optical properties.

### 1.1. Experimental work

A mixture with molar composition: 60TeO$_2$–(30-x)ZnO–5Bi$_2$O$_3$–5TiO$_2$–xB$_2$O$_3$ (where x = 0, 2.5, 5.0, 7.5 and 10.0, hereafter, named as TZBT B0, TZBT B2.5, TZBT B5, TZBT B7.5 and TZBT B10 glasses, respectively) of about 10 grams was prepared and weighed in a glove box. Homogenisation was carried out by grinding the mixture in a mortar for about 20 min. Melting was carried out in a platinum crucible heated in an electrical furnace at a temperature of 900 °C for about 60 min. The melt was stirred periodically in order to obtain a homogeneous glass. Casting was carried out by pouring the melt into a 285 °C pre-heated mould and holding at that temperature for 6 h followed by cooling to room temperature at a cooling rate 1 °C min$^{-1}$. For the purpose of optical characterisation, all samples were polished down to optical quality.

The amorphous nature of TeO$_2$–ZnO–Bi$_2$O$_3$–TiO$_2$–B$_2$O$_3$ glasses was confirmed using XRD with Cu-Kα radiation source with wavelength 1.544 Å, anode current value 35mA and accelerating potential of 40 kV. The scan step was 1° min$^{-1}$ and the scan range for all the glasses were 10° to 80°. Density measurement was carried out at room temperature using a pycnometer employing Archimedes principle, with distilled water as an immersion fluid according to the following equation:

$$\rho_g = \rho_w \frac{m_{pg} - m_p}{(m_{pg} - m_p) - (m_{pgw} - m_{pw})}$$  \hspace{1cm} (1)

where $m_p$, $m_{pg}$, $m_{pgw}$ and $m_{pw}$ are mass of empty pycnometer, mass of pycnometer containing glass, mass of pycnometer containing glass and water, and mass of pycnometer containing water, respectively. Based on the density data, other physical properties such as molar volume ($V_m$), oxygen packing density (OPD), concentration of B$^{3+}$ ions ($C_{B^{3+}}$), polaron radius ($r_p$), inter ionic distance ($d$) and field strength ($F$) can be calculated using the following equations [19–21]:

$$V_m = \frac{\sum x_i M_i}{\rho_g}$$  \hspace{1cm} (2)

$$\text{OPD} = \frac{1000 N_O \rho_g}{M_g}$$  \hspace{1cm} (3)

where $N_O$ is the number of oxygen atoms inside the glass composition, $\rho_g$, density of each glass sample, and $M$ is the molecular weight of the glass.

$$C_{B^{3+}} = \frac{2n_{B_2O_3}N_A\rho_g}{M_g}$$  \hspace{1cm} (4)

Where $n_{B_2O_3}$, $N_A$, $\rho_g$ and $M_g$ are mol fraction of B$_2$O$_3$, Avogadro’s number, density, and average molecular weight of glass, respectively.

$$r_p = \frac{1}{2} \left( \frac{\pi}{6N_{B^{3+}}} \right)^{\frac{1}{3}}$$  \hspace{1cm} (5)

where $N_{B^{3+}}$ is the number of Borate ions per unit volume.

$$d = \frac{1}{2} \left( \frac{1}{N_{B^{3+}}} \right)^{\frac{1}{3}}$$  \hspace{1cm} (6)

$$F = \frac{Z}{r_p}$$  \hspace{1cm} (7)

where, $Z$ is atomic number.

Refractive indices of all samples were measured at room temperature using Brewster’s angle method at wavelength of 632.9 nm while their absorption spectra were recorded at room temperature using UV-Visible Spectrophotometer (Perkin Elmer Lambda 25) at wavelength range 200–1100 nm. Room temperature Raman spectra of all glasses were recorded in the 100–1000 cm$^{-1}$ range using laser working at 632 nm. Thermal characteristics of all TZBTB glasses were determined using DTA (Linseiss type STA PT 1600). In order to obtain
the glass transition temperature ($T_g$), onset of crystallisation temperature ($T_x$), crystallisation temperature ($T_c$), and melting temperature ($T_m$), a scan was recorded at a heating rate of $10^\circ\text{C min}^{-1}$ from 150 $^\circ\text{C}$ to 900 $^\circ\text{C}$.

2. Results and discussion

2.1. Amorphous nature

Five clear glass samples fabricated in this work are shown in figure 1 and their amorphous natures are confirmed with the help of XRD patterns (figure 2). Two broad humps observed around $2\theta = 29^\circ$ and $52^\circ$ along with the absence of sharp peaks as shown in figure 2 confirm the absence of long-range order of atomic arrangement, an atomic arrangement characterising a non-crystalline solid.
more B$_2$O$_3$ is added, the value of tellurite glasses decreases. The decreasing trend of inter B$_3$ concentration, that is from 0.59533 to 2.32249 amu by B$_3$ might be attributed to the decreasing average glass molecular weight, i.e., substitution of Zn$^{2+}$ with Ar = 65.38 amu by B$^{3+}$ with Ar 10.81 amu. Further from figure 3, the molar volume of glass increases with increasing the content of B$_2$O$_3$. The decreasing trend of inter B$_3$ atomic distance is a direct impact of increasing B$_2$O$_3$ concentration, that is from 0.59533 to 2.32249 $\times$ 10$^{21}$ ions cm$^{-3}$ which corresponds to B$_2$O$_3$ concentrations of 2.5 mol% and 10%, respectively. Considering that a crystalline phase has higher density and less molar volume than the corresponding amorphous phase, this result clearly indicates that this substitution results in formation of a highly dense glass structure [22].

Figure 4 is DSC curves obtained for all the investigated glasses recorded at a heating rate of 10 °C min$^{-1}$. Two exothermic crystallization peaks and two melting endothermic peaks caused by melting are clearly seen in glasses containing 2.5 and 5.0 mol% of B$_2$O$_3$ indicating that two crystalline phases were formed upon heating. The first exothermic crystallization peak may due to nucleation process followed by formation of a crystalline phase possessing lower temperature minimum Gibbs free energy while the second peak is due to the formation of higher Gibbs free energy crystalline phase [23].

The values of $T_p$, $T_o$, $T_{c-1}$, $T_{c-2}$, $T_m-1$ and $T_m-2$ for sample containing 2.5 mol% of B$_2$O$_3$ are 349 °C, 415 °C, 429 °C, 480 °C, 705 °C and 760 °C, respectively. The values of $T_p$, $T_o$, $T_m$, thermal stability ($\Delta T = T_m - T_p$) and glass forming tendency ($K_g = \Delta T_p/\Delta T_m$) of all samples are tabulated in table 2. For the cases that several crystallization peaks or melting peaks are observed, only the first peak is used [23]. For many applications requiring to reshape or process a glass at relatively low temperature without fearing the possible formation of a tiny crystalline phase, e.g., in optical fibre drawing, wider $\Delta T$ will provide a flexible choice in determining working temperature. For this purpose, $\Delta T \geq 100$ °C is expected. The value of $\Delta T$ for all samples containing B$_2$O$_3$ ranges from 48 °C to 66 °C which is comparable to that obtained in common fluoride glasses [24, 25], tellurite glasses [26, 27] and borate glasses [28, 29]. TZBTB-2.5 shows the highest $\Delta T$, i.e., $\Delta T = 66$ °C. When more B$_2$O$_3$ is added, the value of $\Delta T$ decreases. $\Delta T$ values of TZBTB-5, TZBTB-7.5 and TZBTB-10 are 57 °C, 53 °C and 48 °C, respectively. These values are less than those reported in other works [30, 31]. In order to provide a flexible working temperature for fibre drawing, commonly accepted criterion for glass stability is $\Delta T \geq 100$ °C.

Table 1. Density, molar volume, OPD, ionic concentration, polaron radius, inter-ionic distances, and field strength values of B$_2$O$_3$ doped TZBT doped glasses.

| Physical properties | TZBT | TZBTB-2.5 | TZBTB-5.0 | TZBTB-7.5 | TZBTB-10 |
|--------------------|------|-----------|-----------|-----------|----------|
| Density (g cm$^{-3}$) | 5.879 | 5.819 | 5.780 | 5.665 | 5.646 |
| Molar Volume (cm$^3$) | 25.083 | 25.293 | 25.409 | 25.877 | 25.909 |
| OPD (mol$^{-1}$) | 69.77 | 71.17 | 72.81 | 73.42 | 75.26 |
| B$_3$ Ionic concentration (1021 ions cm$^{-3}$) | 0.595 | 1.185 | 1.746 | 2.322 |
| Inter B$_3$ Ionic Distance (Å) | 5.599 | 2.813 | 1.909 | 1.434 |
| Field Strength (× 10$^{-15}$ cm$^{-2}$) | 1.113 | 0.281 | 0.129 | 0.073 |

2.2. Density and thermal properties

Table 1 tabulates density and several properties derived from density by following equations (2)–(7). The way the density and molar volume change with B$_2$O$_3$ contents is shown in figure 3. It can be seen that incorporating B$_2$O$_3$ into the glass to partially substitute ZnO results in decreasing density from 5.8791 to 5.6463 g cm$^{-3}$. This result might be attributed to the decreasing average glass molecular weight, i.e., substitution of Zn$^{2+}$ with Ar = 65.38 amu by B$^{3+}$ with Ar 10.81 amu. Further from figure 3, the molar volume of glass increases with increasing the content of B$_2$O$_3$. The decreasing trend of inter B$_3$ atomic distance is a direct impact of increasing B$_2$O$_3$ concentration, that is from 0.59533 to 2.32249 $\times$ 10$^{21}$ ions cm$^{-3}$ which corresponds to B$_2$O$_3$ concentrations of 2.5 mol% and 10%, respectively. Considering that a crystalline phase has higher density and less molar volume than the corresponding amorphous phase, this result clearly indicates that this substitution results in formation of a highly dense glass structure [22].

Figure 4 is DSC curves obtained for all the investigated glasses recorded at a heating rate of 10 °C min$^{-1}$. Two exothermic crystallization peaks and two melting endothermic peaks caused by melting are clearly seen in glasses containing 2.5 and 5.0 mol% of B$_2$O$_3$ indicating that two crystalline phases were formed upon heating. The first exothermic crystallization peak may due to nucleation process followed by formation of a crystalline phase possessing lower temperature minimum Gibbs free energy while the second peak is due to the formation of higher Gibbs free energy crystalline phase [23].

The values of $T_p$, $T_o$, $T_{c-1}$, $T_{c-2}$, $T_m-1$ and $T_m-2$ for sample containing 2.5 mol% of B$_2$O$_3$ are 349 °C, 415 °C, 429 °C, 480 °C, 705 °C and 760 °C, respectively. The values of $T_p$, $T_o$, $T_m$, thermal stability ($\Delta T = T_m - T_p$) and glass forming tendency ($K_g = \Delta T_p/\Delta T_m$) of all samples are tabulated in table 2. For the cases that several crystallization peaks or melting peaks are observed, only the first peak is used [23]. For many applications requiring to reshape or process a glass at relatively low temperature without fearing the possible formation of a tiny crystalline phase, e.g., in optical fibre drawing, wider $\Delta T$ will provide a flexible choice in determining working temperature. For this purpose, $\Delta T \geq 100$ °C is expected. The value of $\Delta T$ for all samples containing B$_2$O$_3$ ranges from 48 °C to 66 °C which is comparable to that obtained in common fluoride glasses [24, 25], tellurite glasses [26, 27] and borate glasses [28, 29]. TZBTB-2.5 shows the highest $\Delta T$, i.e., $\Delta T = 66$ °C. When more B$_2$O$_3$ is added, the value of $\Delta T$ decreases. $\Delta T$ values of TZBTB-5, TZBTB-7.5 and TZBTB-10 are 57 °C, 53 °C and 48 °C, respectively. These values are less than those reported in other works [30, 31]. In order to provide a flexible working temperature for fibre drawing, commonly accepted criterion for glass stability is $\Delta T \geq 100$ °C.
Even though $\Delta T$ of all TZBTB glasses falls below this criterion, re-shaping these glasses into a particular shape at temperature below crystallization temperature, e.g., fibre drawing process, still can be done.

Further from table 2, it can also be seen that $T_g$ increases with increasing B$_2$O$_3$ content. The value of $T_g$ for the base glass (TZBTB-0) is 336 °C. Their values for TZBTB-2.5, TZBTB-5.0, TZBTB-7.5 and TZBTB-10 are 349 °C, 353 °C, 370 °C and 373 °C, respectively. It is known that $T_g$ relates to the minimum energy required to stretch the interatomic bond from a rigid state to a rubbery state where a glass can undergo a relatively large elongation as a relatively small load is applied. It is reported that $T_g$ is linearly proportional to the average bond energy which also means to the average coordination number [32–35] and can be linked to the high network connectivity [36], with network connectivity being defined as the average number of bridging oxygen (BO) atoms connected to a network-forming cation [37]. In such a network, a BO atom is connected to two network polyhedrons. From table 2, it can therefore be expected that glass sample containing higher B$_2$O$_3$ concentration may have higher portion of BO. For this purpose, we have calculated a structural–chemical parameter (NBO/T) defined as the ratio between the number of gram-ions of NBO and the total number of gram-ions of network formers expressed using equation [38, 39]:

**Figure 5.** Relationship between Oxygen Packing density with variation of B$_2$O$_3$ concentration in TZBTB glasses.

**Figure 6.** Trend of decreasing refractive index and density as function of B$_2$O$_3$ concentration.

| Samples    | $T_g$ (°C) | $T_x$ (°C) | $T_c$ (°C) | $T_m$ (°C) | $\Delta T$ (°C) | $K_g$ | BO/NBO |
|------------|------------|------------|------------|------------|----------------|-------|--------|
| TZBTB-0    | 336        | 394        | 451        | 756        | 58             | 0.377 | 0.1    |
| TZBTB-2.5  | 349        | 415        | 429        | 705        | 66             | 0.297 | 0.25   |
| TZBTB-5.0  | 353        | 410        | 422        | 746        | 57             | 0.213 | 0.5    |
| TZBTB-7.5  | 370        | 423        | 436        | 659        | 53             | 0.296 | 1      |
| TZBTB-10.0 | 373        | 421        | 445        | 726        | 48             | 0.256 | 2.5    |

**Table 2.** Glass transformation temperature ($T_g$), Onset crystallisation temperature ($T_x$), Crystallisation temperature ($T_c$), Melting temperature ($T_m$), thermal stability ($\Delta T$) and Glass forming tendency ($K_g$) of all TZBTB glasses with variation of B$_2$O$_3$ concentration.
Where $T$ is total number of gram-ions of network formers, while $N_{MO_i}$ and $X_{MO_i}$ are the number and mol fraction of oxide $M_iO_j$ in glass composition, respectively. Expressed in terms of $BO/NBO$, the results are given in Table 2. $BO/NBO$ ratio increases with the increase of $B_2O_3$ content which is in a good agreement with the increase trend of OPD as the $B_2O_3$ content is increased (Figure 5). Furthermore, the decreases of field strength as shown in Table 1 supports this result. A BO atom carries less negative charge than that of an NBO atom. Consequently, increasing the BO portion in glass results in a decreasing field strength.

2.3. Optical properties

2.3.1. Refractive index

Table 1 gives refractive indices of the studied glasses. Their values decrease with the increase of $B_2O_3$ concentration (the increase of glass density) (Figure 6). Such a density-refractive index relation, which is also reported in other papers [41], can be easily understood from electromagnetic theory. It is known that refractive index ($n$) at an angular frequency $\omega$ can be expressed by the following equation:

$$n^2 = 1 + \chi$$

with

$$\chi = \frac{Ne^2}{m_e\varepsilon_0(\omega_0^2 - \omega^2) + 2\gamma \omega}$$

In this equation, $N$ is electron density, which is the number of electrons bounded by $N$ atomic nuclei per unit volume, $e$ is electric charge, $m_e$ is electron mass, $\gamma$ is damping coefficient, and $\varepsilon_0$ is free space permittivity. Partial substitution of a heavier ion $Zn^{2+}$ (Ar = 65.4 amu) by a lighter ion $B^{3+}$ (Ar = 10.8 amu) means reduction of glass density and thus of $N$ resulting in creating a glass with low refractive index.
Figure 7 depicts how refractive index of the studied glasses relate to \( \text{BO}/\text{NBO} \) ratio. Adding \( \text{B}^{3+} \) with an ionic polarisability 0.002 to partially substitute \( \text{Zn}^{2+} \) with an ionic polarisability of 0.283 causes decreasing glass polarisability. Since a glass having higher \( \text{BO}/\text{NBO} \) ratio is less polarisable than that which has lower \( \text{BO}/\text{NBO} \) ratio [41], any glass compositional changes resulting in increasing this ratio decrease the glass refractive index.

2.3.2. Optical absorption

Figure 8 is the absorption spectra of the studied glasses within the range of 200 nm–1100 nm recorded at room temperature. The absorption edges for all the studied glasses are in position within the range of 436.04 nm–444.45 nm (table 3); covering almost all UV regions, i.e., UVC (100–280 nm), UVB (280–315 nm) and UVA (315–400 nm); suggesting that these glasses could be used as good UV-shielding materials [42, 43]. As shown in the inset, the absorption edges are red shifted as \( \text{B}_2\text{O}_3 \) concentration is increased from 2.5 mol% to 10 mol%.

The energy gap values for all samples can be calculated using the Davis and Mott equation [44]:

\[
\alpha h\nu = B(h\nu - E_g)^m
\]  

where \( \alpha \) is absorption coefficient, \( B \) is a constant called the tail band parameter, \( h \) is Planck’s constant, \( \nu \) is frequency of light, and \( m \) can take the values of 1/3, 1/2, 2 or 3 which is determined by the type of electronic

| Sample Code | \( \lambda_c \) (nm) | \( E_{gap} \) (eV) | \( E_u \) (eV) | \( n \)       |
|-------------|---------------------|------------------|--------------|-------------|
| TZBTB 0     | 436.04              | 2.657            | 0.365        | 1.875 ± 0.015 |
| TZBTB 2.5   | 437.48              | 2.669            | 0.370        | 1.766 ± 0.020 |
| TZBTB 5     | 439.12              | 2.674            | 0.368        | 1.758 ± 0.017 |
| TZBTB 7.5   | 441.79              | 2.701            | 0.367        | 1.751 ± 0.011 |
| TZBTB 10    | 444.45              | 2.725            | 0.366        | 1.741 ± 0.021 |

Figure 9. Optical band gap of TZBTB Glass sample with variation the \( \text{B}_2\text{O}_3 \) content.

Figure 10. Refractive index of all the investigated glasses as function of band gap energy.
transition. For amorphous materials, the suggested value of $m$ for the allowed transition is 2 while that for the prohibited transition is $2/3$. The value of $E_{gap}$ is obtained by extrapolating the linear portion of $(\alpha h\nu)^{1/2}$ versus $h\nu$ as shown in figure 9 and the results are tabulated in table 3. $E_{gap}$ increases with the increases of B$_2$O$_3$ concentration and thus to the ratio of BO/NBO (figure 7). Similar results have also been reported in other works [45, 46]. Increasing the amount of BO portion creates a more compact network and this leads to the lowering of the top of the valence band resulting in the increase of $E_g$ [46, 47].

Linked to refractive index as discussed in previous sub-section, it is clearly seen that refractive index and $E_{gap}$ respond conversely to the change of BO/NBO ratio. For all the investigated glasses, such relation is shown in figure 10 and is best fitted using equation:

$$n = n_0 + A_1 \exp \left( -\frac{E_{gap} - E_{gap,0}}{t_1} \right)$$

(12)

Where $n_0$, $E_{gap,0}$, $A_1$, and $t_1$ are constants. For the investigated samples, their values are 1.74615, 2.65687, 0.13139 and 0.00667, respectively. This typical change of refractive index versus band gap energy has also been reported in other papers but expressed in different approaches [48–53]. Moss’s formulation [52] for this relation is expressed as:

$$n^4E_{gap} = 95 \text{ eV}$$

(13)

This equation was then modified by Reddy and Ahamed [53] as:

$$n^4(E_{gap} - 0.365) = 154$$

(14)

A refractive index-energy bandgap relationship similar to that obtained in this work (equation (12)) was proposed by Kumar et al [51]:

$$n = K_1 e^{-K_2E_{gap}}$$

(15)

where $K_1$ and $K_2$ are constant. Whatever the approach [51–53], it can be seen that refractive index decreases with the increase of band gap energy. Applying equations (14) and (16) to the refractive index and band gap energy data available in [48–53], it suggests that constant values apply only to a glass host experiencing compositional change and not to relate refractive index and band gap energy values taken from combined different glass hosts.

2.3.3. Urbach energy

Further from figure 8, it can be seen that the spectral absorption near the UV absorption edge dropped exponentially with the increase of wavelength. Expressing the absorption coefficient ($\alpha$) in terms of phonon energy ($h\nu$), it was shown that such change follows the empirical Urbach’s rule [54] expressed by

$$\alpha(\nu) = \alpha_0 \exp \left( \frac{h\nu}{E_u} \right)$$

(16)

where $\alpha_0$ is a constant and $E_u$ is the width of Urbach energy, the width of the band tail energy near the fundamental absorption edge arising from static disorder of glass structure or the extent of band tail in electronic density state in the region of the forbidden energy gap [47, 55, 56]. Figure 11 presents the plot of In$\alpha$ as function of photon energy ($h\nu$). Urbach energy value can be calculated by finding the gradient (slope) from the linear region on the curve at lower phonon energy values. The Urbach energy of the glass containing 0 mol% of B$_2$O$_3$ is 0.365 eV. As 2.5 mol% of B$_2$O$_3$ is added, its value becomes 0.370 eV. Its value then decreases as the B$_2$O$_3$ concentration is increased, opposite to the way the band gap energy ($E_{gap}$) change as B$_2$O$_3$ concentration is
increased. These two results (increasing band gap and decreasing Urbach energy) suggest that adding B$_2$O$_3$ into the glass creates a more compact network and the glass structure becomes less disordered [57]. This result is consistent to the finding that the BO/NBO ratio increases with the increase of B$_2$O$_3$ concentration.

2.3.4. Raman spectra

Figure 12(a) is Raman spectra of the studied glasses in the range of 100–1000 cm$^{-1}$. The broad band observed in all spectra is attributed to the amorphous nature of glass. In all glasses, four distinctive bands located around 415 cm$^{-1}$, 440 cm$^{-1}$, 650 cm$^{-1}$ and 725 cm$^{-1}$ are observed. As shown by red arrow, the peak of the second hump shifts to higher wave number as B$_2$O$_3$ concentration increase. To discuss the effect of increasing B$_2$O$_3$ concentration on structural unit composing the glasses further, deconvolution of all bands into component bands was carried out for all Raman spectra (figures 12(b)–(f)). Deconvolution was carried out by varying the number of peaks until the maximum value of $R^2$ is obtained. For each spectrum, eight component bands are obtained.

The component band with peak in the range of 736–740 cm$^{-1}$ may be attributed to the stretching vibrations in TeO$_3$ and TeO$_{3+1}$ groups [58, 59], that is stretching vibration between Te and non-bridging oxygen ions in
TeO$_{3+x}$ unit [60]. The band located around 651–642 cm$^{-1}$ may be attributed to symmetric and anti-symmetric stretching vibration modes of TeO$_4$ units that form a continuous network [60, 61]. The band located at around 598–630 cm$^{-1}$ may be attributed to Te–O stretching vibrations mode in TeO$_4$ [62]. The fourth band located around 466–481 cm$^{-1}$ may be assigned as symmetric stretching and bending vibrational mode of Te–O–Te linkages [59, 63]. The fifth around 446–406 cm$^{-1}$ is assigned as symmetrical stretching or bending vibration of Te–O–Te linkages at corner sharing sites [64]. The sixth band at around 366–334 cm$^{-1}$ may be attributed to symmetric stretching vibration of Bi–O atoms or stretching vibration of Bi–O–Bi [1, 65]. The last two bands 287–250 cm$^{-1}$ and 212–206 cm$^{-1}$ may be attributed to vibrational mode of Te$_2$ based nanoclusters [66, 67], respectively.

Finally, it can be seen from figure 12 that the maximum phonon energy [68–71] of all the examined glasses are nearly the same, which are in the range of 736–740 cm$^{-1}$. These values are slightly lower than most of tellurite glasses [63, 72] but significantly lower than silicate glasses [73, 74], borate glasses [75], phosphate glasses [76]. Having such low phonon energy, doping rare earth ions in the examined glasses can result in low multi-phonon relaxation rate and therefore increase luminescence efficiency [69, 71]. These glasses can therefore be considered as a good glass matrix for fluorescent ions like Nd$^{3+}$, Tm$^{3+}$, etc.

3. Conclusions

Clear and free crystalline glasses with compositions of 60TeO$_2$–(30–x) ZnO–5Bi$_2$O$_3$–5TiO$_2$–xB$_2$O$_3$ with x = 0, 2.5, 5.0, 7.5 and 10.0 mol% have been successfully fabricated. The effect of addition of B$_2$O$_3$ on density, oxygen packing density, glass transition temperature, glass stability, BO/NBO ratio, band gap energy, refractive index, field strength, Urbach tail energy and phonon energy have been studied. As B$_2$O$_3$ increased from 0 to 10 mol%, density changed from 5.879 to 5.646 g cm$^{-3}$, field strength 1.113 to 0.072 (10$^{-13}$ cm$^{-2}$), oxygen packing density 69.77 to 75.26 mol$^{-1}$, BO/NBO ratio 0.1 to 2.5, refractive index 1.875 to 1.741 and band gap energy 2.657 to 2.725. Glass containing 2.5% of B$_2$O$_3$ shows the highest glass thermal stability ($\Delta T = 66 ^\circ C$), which still below commonly accepted criterion for glass stability ($\Delta T \geq 100 ^\circ C$). By carefully control the operating temperature of fibre drawing process, fabricating fibre optic from TZBTTB glass is still affordable and very challenging especially if it is related to their low phonon energy which is in the range of 736–740 cm$^{-1}$.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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