Bismuth modified physical, structural and optical properties of mid-IR transparent zinc boro-tellurite glasses

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Tellurium oxide based quaternary glasses in the system TeO₂, B₂O₃, Bi₂O₃, ZnO have been prepared by melt quenching technique. Amorphous nature of the samples has been ascertained by X-ray Diffraclagram. The values of density and molar volume increase with increase in Bi₂O₃ content. Theoretical calculations of crystalline volume (Vc) have also been made. The glass transition temperature (Tg) has been determined using differential scanning calorimetry (DSC) and its value is observed to decrease with increase in Bi₂O₃ content. IR and Raman spectra of the present glass system indicate that ZnO acts as network modifier and exists in TeO₃ structural units and the number of TeO₄ structural units into TeO₃ structural units and the number of TeO₄ groups decreases with increase in bismuth content except for the glass sample with x = 5, which shows maximum number of TeO₄ structural units among all other studied glass samples and transformation of some of TeO₄ structural units into TeO₃ structural units is observed with increase in bismuth content. Bismuth plays the role of network modifier with BiO₆ octahedral structural units for glass samples with x = 5, 10, and 15, whereas, exists in network forming BiO₃ trigonal and BO₃ tetrahedral structural units. The transmittance of the present glasses is observed to be very high (up to 95%) in the spectral range (λ = 2.5–6.5 μm) which is of great technological importance. The percentage value of transmittance increases with increase in Bi concentration. The Hydrogenic excitonic model is applicable to the presently studied glasses and the optical band gap energies (Eg) calculated from this model and Tauc’s plots for direct transitions are almost same. Eg decreases with increase in bismuth content, however, the molar refractivity (Rm) show the reverse trend. Metallization criterion for these materials shows that these glasses may be potential candidates for non linear applications.

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1. Introduction

Because of high transparency in the middle infra red (MIR) and near infra red (NIR) regions, tellurium based oxide and chalcogenide glasses have potential applications in civil, medical and military areas such as in thermal imaging, chemical sensing, laser fiber amplifiers, infrared laser power delivery, missile dome, windows of the laser radar, atmospheric transmission windows, aerial reconnaissance and surveillance [1,2]. It is known that pure TeO₂ cannot form glass except under particular extreme conditions [3]. The addition of various oxides increases the glass forming range of tellurites [4]. The structural and physical properties of tellurite and boro-tellurite glasses have been intensely studied for their scientific interest and practical applications [5,6]. Addition of ZnO to boro tellurite glass network produces stability and increasing glass forming ability [7]. Glasses containing Bi₂O₃ and ZnO have a long infrared cut off and third order non linear optical susceptibility which make them ideal candidate for application as infra red transmission components and photonics devices [8,9]. Recently, addition of oxides of heavy metals such as Bi₂O₃, Nb₂O₅, to tellurite glasses is being taken up for studies as such addition enhances both the physical and the optical properties of these glasses [10]. A review of literature indicates that there are many reports on TeO₂-B₂O₃ [11,12], TeO₂-B₂O₃-ZnO [13,14], TeO₂-ZnO [15,16] Bi₂O₃-B₂O₃-ZnO [17–21] glass system, but there is hardly any systematic study on TeO₂-B₂O₃-B₂O₃-ZnO glass system. The aim of the present paper is to study the effect on Bismuth on the physical, structural and optical properties of mid-IR transparent tellurium based quaternary glasses.

2. Experiment

Glass samples of compositions 60 TeO₂ xBi₂O₃ (30–x) B₂O₃ 10ZnO; x = 0, 5, 10, 15 and 20 were prepared by conventional rapid melt quenching technique. The appropriate amounts of TeO₂, ZnO, Bi₂O₃, and H₃BO₃ are thoroughly mixed in an agate pestle-mortar. Silica crucible containing the mixture was put in an electrically heated muffle furnace and the temperature was raised slowly to 750–800 °C depending on the composition. This temperature was maintained for about
30 min and the melt was shaken frequently to ensure proper mixing and homogeneity. The melt was then poured onto a specially designed stainless steel block and was immediately pressed by another stainless steel block at room temperature. Density ($\rho$) of the samples was measured to an accuracy of 0.001 by Archimedes’ principle using xylene as immersion liquid. X-ray diffraction studies of the samples were performed by using Rigaku Table-Top X-ray Diffractometer at a time scan of 2 deg/min. The values of glass transition temperature ($T_g$) of different samples were measured by DSC technique using TA Instruments, Model no. Q600 SDT, at a heating rate 10 °C/min in nitrogen atmosphere. The Fourier Transform Infra Red (FTIR) spectra of the glass samples were recorded at room temperature using Shimadzu IR affinity-1 8000 FTIR spectrophotometer in the wavelength range 4000–400 cm⁻¹. The powdered samples were thoroughly mixed with dry KBr in the ratio 1:20 by weight and then pellets were formed under a pressure of 9–10 tons. The Raman spectra were recorded using Renishaw Invia Reflex Micro Raman Spectra with Ar ion laser (514 nm) under back scattering configuration. The room temperature absorption spectra of the glass samples were recorded using Carry 5000 double beam UV–visible spectrophotometer in the wavelength range 200–800 nm. The peak fitting and non-linear curve fitting of experimental data have been done by using Origin Pro 8.6 software.

3. Results

3.1. XRD

The X-ray diffraction patterns of the as-prepared glass samples show only broad diffuse scattering at low angles. This type of scattering is the characteristic of long range structural disorder and the amorphous nature of the glass samples in the studied composition range [7].

3.2. Density

The values of density ($\rho$) measured for all the samples using Archimedes’ principle are given in Table 1. Perusal of the data presented in Table 1 shows that the density of samples increases with increase in Bi₂O₃ content. This increase in density is expected in the present system as lighter Bi₂O₃ is being increasingly replaced by heavier Bi₂O₃. The molar volume ($V_m$) of samples was calculated using the following relation [22]

$$ V_m = \sum x_i M_i / \rho $$

where $x_i$ is the molar fraction and $M_i$ molecular weight of the $i$th component and $\rho$ is the density of the sample. The values of $V_m$ so calculated are given in Table 1. The molar volume increases with increase in bismuth content [23]. The same type of behavior has also been reported by various other researchers [21,24]. Crystalline volume ($V_c$) of the glass samples given by formula [24]

$$ V_c = \sum x_i V_i $$

where $V_i$ is the molar volume of $i$th component in crystalline phase (i.e. $V_i$ = 28.148, 24.247, 52.357 and 14.516 cm³/mole for $\alpha$-TeO₂, Bi₂O₃, Bi₂O₅ and ZnO by taking crystalline density 5.670, 2.55, 8.90 and 5.606 gm/cm³ for $\alpha$-TeO₂, Bi₂O₅, Bi₂O₅ and ZnO respectively).

The calculated values of $V_c$ are also included in Table 1. The data of molar volume and crystalline volume have been plotted in Fig. 1 for comparison. Perusal of the data plotted in Fig. 2 show that the $V_m$ of the glasses for $x = 0$, 5, 10, 15 and 20 is always greater than the corresponding values of $V_c$, indicating the presence of excess structural volume in these samples; this is characteristic of their glassy nature [24].

3.3. Differential scanning calorimetry

The results of differential scanning calorimetry (DSC) for 60 TeO₂-xBi₂O₅-(30-x)Bi₂O₅:10ZnO glass samples are shown in Fig. 2. The glass transition temperature ($T_g$) has been estimated from the minima occurred in the graph between dH/dT versus temperature. The inset plot in Fig. 2 showing plot between dH/dT and temperature for glass sample $x = 0$. Perusal of data presented in Fig. 2, it is observed that the crystallization peaks are not detected in the studied temperature range for the studied glass compositions except for the composition with $x = 20$. Oxygen packing density (OPD) which is a measure of the tightness of packing of the oxide network was calculated using the following relation [20]

$$ OPD = (\rho / M) \times n $$

where $M$ is molecular weight ($M$) and $n$ is the number of oxygen atoms per formula unit. Higher the value of OPD; more will be the tightness of packing.

Values of oxygen packing density (OPD) so obtained and that of glass transition temperature ($T_g$) measured using DSC are shown in Table 1. Fig. 3 shows variation of $T_g$ and OPD with concentration of Bi₂O₃. Perusal of the data presented in figure shows that glass transition temperature exhibits a non linear variation with maximum $T_g$ for glass sample with $x = 5$, whereas, there is an overall decrease in $T_g$ with the increase in Bi₂O₃ content. Such type of variation is also observed by other researchers [25]. This behavior in $T_g$ with bismuth content is due the change in structure of TeO₂ in the presently studied glass compositions, which is explained in the Raman and FTIR studies section. Oxygen packing density may also be used to explain the decrease in $T_g$ with increase in the Bi₂O₃ content. The oxygen packing density is found to decrease with increase in bismuth concentration (Fig. 3) showing that the structure becomes loosely packed (i.e. less tightness of packing). A loosely open packed structure requires smaller internal energy for the chain mobility needed for glass transition. So, addition of Bi₂O₃ indicates the formation of more open macromolecular chain which leads to decrease in $T_g$ [20].

![Fig. 1 Variation of molar volume ($V_m$) and crystalline volume ($V_c$) with Bi₂O₃ content ($x$) for 60 TeO₂-xBi₂O₅-(30-x)Bi₂O₅:10 ZnO glass system.](image-url)
Fig. 2. DSC curves for different compositions of 60 TeO$_2$xBi$_2$O$_3$ (30–x) B$_2$O$_3$ 10 ZnO glass system.

Fig. 3. Variation of oxygen packing density (OPD) and glass transition temperature ($T_g$) with Bi$_2$O$_3$ content (x) for 60 TeO$_2$xBi$_2$O$_3$ (30–x) B$_2$O$_3$ 10 ZnO glass system.

Fig. 4. Raman spectra for different glass compositions of 60 TeO$_2$xBi$_2$O$_3$ (30–x) B$_2$O$_3$ 10 ZnO glass system at room temperature.

3.4. Raman spectra

The Raman spectra of 60 TeO$_2$xBi$_2$O$_3$ (30–x) B$_2$O$_3$ 10ZnO glass system recorded at room temperature in the spectral range 100–2000 cm$^{-1}$ is shown in Fig. 4. The peaks in the Raman spectra have been estimated by deconvolution of the spectra and typical deconvoluted spectra exhibits several peaks and peak position, amplitude and full width half maximum of these peaks are presented in Table 2. The Raman spectra consist of three pronounced peaks that occur at around 750–760 cm$^{-1}$, 660–670 cm$^{-1}$, 450–390 cm$^{-1}$ and four small peaks at around 55–110 cm$^{-1}$, 255 cm$^{-1}$ and 820–850 cm$^{-1}$ and 1350–1375 cm$^{-1}$ respectively.

3.5. IR spectra

The room temperature Fourier transforms infrared spectra of 60 TeO$_2$xBi$_2$O$_3$ (30–x) B$_2$O$_3$ 10ZnO glass compositions recorded in spectral range 400–1400 cm$^{-1}$ are displayed in Fig. 6a. The FTIR spectra of the glass samples in the spectral range 400–1500 cm$^{-1}$ have been deconvoluted and a typical deconvoluted spectra for $x = 20$ is shown in Fig. 6b. The deconvoluted spectra exhibit several peaks and peak position, amplitude and full width half maximum of these peaks are presented in Table 3.

3.6. Optical absorption spectra

IR spectra shows that as the bismuth content increases from $x = 0$ to $x = 20$ the transmittance is observed to increase from 60% to 95% in the mid IR range 2.5–6.5 μm, as shown in Fig. 7.

The UV–vis absorption spectrum of the present glass samples have been taken at room temperature. The absorption coefficient was determined from the relation [14]

$$a(\nu) = A/t$$

where $A$ is the absorbance and $t$ is the thickness of the sample. The absorption coefficient, $a(\nu)$ and optical band gap energy, $E_g$, in many amorphous materials are related as [24]

$$zhv = A(hv - E_g)^m$$

where $x$ is the absorption coefficient, $h\nu$ is the incident photon energy, $A$ is constant, $E_g$ is the optical band gap energy and the exponent $m$ is a parameter which depends on the type of electronic transition responsible for absorption. It has different values viz. 1/2, 2, 1/3, and 3 corresponding to direct allowed, indirect allowed, direct forbidden and indirect forbidden transitions, respectively. The band gap energies of different glass samples are estimated by extrapolation of linear region of the curves to meet $h\nu$ axis i.e. where $zhv^2 = 0$ and the values so obtained are listed in Table 1. Change in $(zhv)^2/m$ with $h\nu$ called Tauc’s plot has been plotted for $m = 1/3$, 1/2, 2 and 3 but $m = 1/2$ is found to be most suitable and Tauc’s plot for $m = 1/2$ is shown in Fig. 8. Thus, the present glass system shows direct allowed transitions.

The shape of absorption spectrum of the present glass system is like that for the Hydrogenic excitonic model provided an explicit expression for the optical absorption due to bound and continuum excitons [26,27]. An exciton is the bound state between an electron in the conduction band and a hole in the valence band. The basic assumptions of the model are: (1) the bands are parabolic; (2) transition momentum matrix elements between single-particle states are constant throughout the Brillouin zone. Accordingly, the excited states of an exciton can be considered as in hydrogen-atom-like model. Intrinsic parameters such as band gap ($E_g$) and excitonic binding energy ($R$) can be determined by fitting the
absorption spectrum with an appropriate analytical model. The absorption coefficient \( \alpha \) introduced by Hydrogenic excitons model is given as

\[
\alpha(E) = \frac{C_0 R^{1/2}}{E} \left\{ \sum_{m=1}^{\infty} \frac{2R}{m^2} \frac{\Gamma_m}{(E - E_m)^2 + \Gamma_m^2} + \frac{\Gamma_c}{2} \left[ \pi \frac{\arctan \left[ \frac{\hbar \nu - E_c}{E_c} \right]}{\gamma} + \frac{\pi}{2} \sinh(2\nu^c) - \cos(2\nu^c) \right] \right\}
\]

with

\[
\nu^c = \frac{\pi R^{1/2}}{2} \left[ \frac{(E - E_{c1}^2 + \Gamma_{c1}^2)}{E - E_{c2}^2 + \Gamma_{c2}^2} \right]^{1/2}
\]

and \( \Gamma_m = \Gamma_c - (\Gamma_c - \Gamma_1^m)/m^2 \), \( m = 1, 2, 3 \).

where \( C_0 \) is the absorption strength parameter, \( E \) is the incident photon energy and \( \Gamma_1 \) and \( \Gamma_c \) are the line widths of the \( m = 1 \) state and of the continuum, respectively. Near the band edge, the first term gives rise to a single peak centered at energy \( E_m \) and approximately of width \( \Gamma_1^m \). The rest of the terms represent the excitonic continuum and yield a step like absorption edge of width \( \Gamma_c \) above the band gap [27]. As shown in Fig. 9, the experimental data fitted with Hydrogenic excitonic model (Eq. (6)) gives very good fitting with best fit parameter \( R^2 \) in range 0.987–0.997. The values of parameters \( C_0, R, \Gamma_1, E_c \) and \( \Gamma_c \) have been estimated from the fitting of experimental data with the Hydrogenic excitonic model and are listed in the Table 4.

The amorphous materials such as glasses consist of band tailing in the forbidden energy gap arising from random fluctuations of the internal disorder in the amorphous materials. The Urbach energy was used to characterize the degree of the disorderness in amorphous and crystalline solids. So, it can be estimated using the following Urbach equation [28]

![Fig. 5. Deconvoluted Raman spectra for 60 TeO_2:20Bi_2O_3:10 B_2O_3:10 ZnO glass system.](image)

![Fig. 6. (a) FTIR spectra for different glass compositions in spectral range 400–1500 cm\(^{-1}\) and (b) deconvoluted IR spectra for 60 TeO_2:20Bi_2O_3:10 B_2O_3:10 ZnO glass system for \( x = 20 \).](image)
where \( B \) is constant and \( \Delta E \) is the width of the band tail of the electron states. The relation (6) can be rewritten as:

\[
\ln(\alpha) = h\nu/\Delta E + \text{constant}
\]

The Urbach energy has been calculated by determining the slope of the linear region of the curve plotted between \( \ln(\alpha) \) and \( h\nu \).
and TeO6 group [32]. This pyramidal and/or BiO6 units from varied types of borate causes increase in TeO3 structural units [41, 42]. The intensity of this band grows continuously among all other studied structural units [7, 13, 31, 45]. The peak observed at 55–60 cm−1 in all the glass samples is attributed to B–O stretching vibrations in BO3 structural groups [46]. The intensity of this band first decreases for x = 5 and then it continuously increasing with increase in x (i.e. Bi2O3 content). It indicates that Te–O–Te bridges between four co-ordinate tellurium atoms in TeO3 structural units, this may be the reason for having maximum value of glass transition temperature.

The Raman peak at 820–850 cm−1 may also be attributed symmetric breathing vibrations of six membered boroxol rings B3O6 with one or two BO3 triangles replaced by BO4 tetrahedron [49]. The decrease in intensity of this band with decrease in B2O3 (increase in x) keeping TeO2 constant supports the assertion of presence of structural units due to both B2O3 and TeO2. The bands occurring in the spectral range 1350–1375 cm−1 may be assigned to B–O vibrations of the units attached to large segments of the borate network [50]. The IR band observed in the region 914–1152 cm−1 is attributed to the B–O–B bending vibrations in the Bo4 tetrahedral structural units [13]. This broad band is observed to split into various peaks as given in Table 3 can be assigned to the stretching vibrations of B–O–B bending vibrations in BO4 structural units from tri-tetra and penta borate groups [51]. The band observed in the range 1212–1473 cm−1 can be assigned to the stretching vibrations of the B–O bond in the Bo3 trigonal structural units [52, 53]. The peaks observed in the range 1212–1370 cm−1 can be assigned to the B–O stretching vibrations in BO3 units from boroxol ring and from 1422 to 1473 cm−1 is attributed to B–O stretching vibrations in BO3 units from varied types of borate groups [54].

With increase in bismuth concentration, the Raman peak observed at 450 cm−1 shifted towards lower wave number side and occurs at 394 cm−1 for x = 20. This peak corresponds to the Bi–O–Bi vibrations in both Bo3 pyramidal and/or Bo6 octahedral structural units [55]. An IR band observed at around 860 cm−1 in the glass composition with x = 5, 10 and 5 may be attributed to Bo6 octahedral structural units [56, 57]. However, the peak observed at 846 cm−1 for the glass composition x = 20 indicates the presence of Bo3 pyramidal structural units [58, 59]. Hence, bismuth acts as a modifier for glass composition x = 5, 10, 15 and network former for x = 20.

Taking into account these structural changes, increase in the concentration of bismuth in the glass structure leads to the following: (i) ZnO acts as network modifier and exists in ZnO4 structural units (ii) the number of TeO3 groups decreases with increase in bismuth content except for the glass sample with x = 5, which shows maximum number of TeO3 structural units among all other studied glass samples and transformation of some of TeO3 structural units into TeO2 structural units is observed with increase in bismuth.
content (iii) bismuth plays the role of network modifier with BiO₆ octahedral structural units for glass samples with x = 5, 10, and 15, whereas, exists in network forming BiO₃ pyramidal structural units for glass sample with x = 20 (iv) there occurs disintegration of some boroxol units and their transformation into tetrahedral BO₄ and trigonal BO₃ structural units.

4.2. Optical absorption spectra
Perusal of data presented in Fig. 7, it is observed that the presently studied glass samples shows maximum transparency in the mid IR region and on addition of Bi₂O₃, the transparency increases and the distortion in the spectra is reduced. These may therefore, be treated as the novel materials transmitting in mid-infrared (MIR) spectral region which are highly desirable for a variety of military and civilian appliances including super continuum generation, infrared countermeasures (IRCM), and MIR laser sources.

The optical band gap energy (Eg) is found to decrease with increase in bismuth content. The shift of the absorption edge is also observed and it is due to structural rearrangements of the glass network and modifier. The shift of the absorption edge and decrease of Eg may be attributed to the progressive increase in the concentration of non-bridging oxygen (NBO) atoms [60]. Perusal of data presented in Tables 1 and 4, it is observed that the values of optical band gap energy estimated from Tauc's plot for direct transitions and fitting of Eq. (6) with experimental data are in good agreement. Therefore, it may be concluded that the direct transition is most probable transition in the present glass system. The values of fitting parameters Cₒ, R, Γₒ and Γᵣ are in good agreement as reported earlier [27]. The small values of exciton binding energy (R), listed in Table 4, leads to increase the spatial separation between the electron and hole reducing the coulomb interaction between them [61]. The values of the Urbach energy for a range of amorphous semiconductors are reported to lie in the range 0.045–0.66 eV [62]. For the present glasses the value of Urbach energy lies between 0.32 and 0.58 eV i.e. within the reported range. Thus the observed values are consistent with the reported values in the literature [63]. In the present system, the Urbach energy is found to decrease with increase in the bismuth content which in turn indicates that the defect concentration is less. The molar refractivity increases with increase in the bismuth content as the molar refractivity (Rm) is directly proportional to the polarizabilities of the constituent ions of the glass which in turn increases with bismuth content. Oxides glasses with good optical non-linearity are reported to possess a metallization criterion of approximately 0.35–0.45. It has also been observed that the studied glass samples possess a metallization criterion in the range 0.422–0.398 (listed in Table 1) and hence the materials under investigation may be considered as new non linear optical materials [11].

5. Conclusions
Quaternary bismuth boro-zinc tellurium glasses have been successfully synthesized by melt quenching technique. The amorphous nature of the glass samples is confirmed by the XRD patterns. It is observed that the density and molar volume increase with increase in Bi₂O₃ content and the same trend is followed by the crystalline volume. Oxygen packing density is found to increase while the glass transition temperature decreases with increase in bismuth content. Raman and FTIR and Raman spectra indicate that ZnO acts as network modifier and exists in ZnO₃ units. TeO₂ exists as TeO₃, TeO₄, and TeO₆ structural units and the number of TeO₄ groups decreases with increase in bismuth content except for the glass sample with x = 5, which shows maximum number of TeO₄ structural units among all other studied glass samples and transformation of some of TeO₄ structural units into TeO₃ structural units is observed with increase in bismuth content. Bismuth plays the role of network modifier with BiO₆ octahedral structural units for glass samples with x = 5, 10, and 15, whereas, exists in network forming BiO₃ pyramidal structural units for glass sample with x = 20. Bi₂O₃ exists in the form of BO₃ trigonal and BO₄ tetrahedral structural units. IR studies revealed that the transmittance increases up to 95% in the mid infra red range (λ = 2.5–6.5 μm) with increase in Bi₂O₃ content. These may therefore, be the good candidates for a variety of military and civilian appliances including super continuum generation, infrared countermeasures (IRCM), and MIR laser sources. The optical band gap energy calculated from Tauc’s plots and Hydrogenic excitonic model decreases with increase in bismuth content, whereas, molar refactivity show the reverse trend. The Urbach energy is found to decrease with increase in the bismuth content indicating that the decrease in defects concentration. The glass compositions under investigation may be considered as new non linear optical materials.

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References
**ZnCl₂ Modified Physical and Optical Properties of Barium Tellurite Glasses**

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The optical properties of tellurite based glass systems are composition dependent. For this purpose glass samples of the composition 70TeO₂-(30–x)BaO-xZnCl₂ with x = 5, 10, 15, 20 and 25 have been synthesized by rapid melt quenching technique. Glassy nature has been confirmed by X-ray diffraction pattern. The physical properties like density, molar volume and crystalline volume have been estimated and found that density decreases while the molar volume increases with increase in ZnCl₂ content. The glass transition temperature decreases with increase in halide content due to increase in the non-bridging oxygen contribution. Direct allowed optical transitions are favourable in these glasses and the optical band gap energy (E_g) has been observed to increase with increase in ZnCl₂ content. The value of Urbach energy of these glasses shows increasing behaviour with ZnCl₂ concentration indicating the breaking of weak bonds into defects. Metallization criterion for these materials shows that these glasses may be potential candidates for non linear applications.

[Keywords: Amorphous, Melt quenching technique, Non-bridging, DSC, UV-Vis spectroscopy]

**Introduction**

Heavy metal oxide (HMO) and oxyhalide glasses have received attention for their interesting properties and potential applications in optical fibres and non linear optics. Among HMO, tellurite glasses have been intensive because of their technological and scientific importance. Tellurite glasses attract much attention from both fundamental and applied research because the glass phase can be formed over a wide range of concentration in addition to its unique properties such as stability at low temperature, good thermal, optical and electronic properties. It has superior properties such as high refractive index, high dielectric constant, wide band infrared transmittance and large third order non linear optical susceptibility. It is known that pure TeO₂ cannot form glass except under particular extreme conditions. Addition of various materials increases the glass forming range of tellurites. Addition of barium oxide into tellurite glasses increases the transition temperature and improves the thermal stability of the network. Tellurite glasses containing barium oxide are used in fiber and Raman gain applications. Pure metal halide glasses are hygroscopic in nature, but when they are added to tellurite glasses their hygroscopic behaviour decreases which limits the application of many pure halide glasses. The choice of tellurite oxyhalide glass system is of particular interest because of their chemical durability, thermal stability and high transmission in IR range. Therefore, the objective of the current work is to study the effect of ZnCl₂ on physical and optical properties of barium tellurite glass systems.

**Experimental**

Glass samples of compositions 70TeO₂-(30–x)BaO-xZnCl₂ (x in mol% and ranging from 5 to 25 in steps of 5) were prepared by conventional rapid melt quenching technique. The appropriate amounts of AnalR grade chemicals TeO₂, BaO and ZnCl₂ were thoroughly mixed in an agate pestle mortar. Silica crucible containing the mixture was put in an electrically heated muffle furnace and the temperature was raised slowly to 750-800°C depending on the composition. This temperature was maintained for 30 min and the melt was stirred frequently to ensure proper mixing and homogeneity. The melt was then poured onto a stainless steel block and was immediately pressed by another stainless steel block at room temperature. X-ray diffraction studies of the samples were performed by using Rigaku Table-Top X-ray diffractometer. Density (ρ) of the samples was measured by Archimedes’ principle using xylene as the immersion liquid. Molar volume was calculated from the molecular weight (M) and density (ρ). Glass transition temperatures (T_g) of different samples were measured by DSC technique using TA Instruments, model no. Q600 SDT, at a heating rate 10°C.min⁻¹ in nitrogen atmosphere. The room temperature absorption spectrum was recorded using Shimadzu UV-3600 double beam UV-Vis-NIR spectrophotometer.

**Results and Discussion**

The XRD patterns of barium oxychloro tellurite glass samples are shown in Fig. 1. Perusal of the data shown in Fig. 1 reveals that all the glass samples exhibit a broad hump and no sharp peaks, indicating the amorphous nature of these samples.

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The density (\(\rho\)) of the samples has been measured by Archimedes’ principle using xylene as the immersion liquid (0.865 g.cm\(^{-3}\)).\(^{24}\) The obtained values of the density and molar volume (\(V_m\)) have been presented in Table I. It is observed that density of the samples decreases with increase in ZnCl\(_2\) content, which may be due to replacement of lighter ZnCl\(_2\) with heavier BaO molecules.\(^{25}\) These results are in good agreement with Mallawany et al.\(^{26}\) for other halogen based glasses. The molar volume increases with increase in ZnCl\(_2\) content. The slight increase in the molar volume may be due to the rearrangement of the lattice and decrease in porosity of the glass.\(^{27}\) Crystalline volume of the glass samples (\(V_c\)) is given by the formula:\(^{28}\)

\[
V_c = \sum x_i V_i
\]

where \(V_i\) is the molar volume of the \(i\)-th component in the crystalline phase and its calculated values are listed in Table I. The values of molar volume and crystalline volume have been plotted in Fig. 2 for comparison. Perusal of the data plotted in Fig. 2 shows that \(V_m\) of the glasses is greater than the corresponding values of \(V_c\) indicating the presence of excess structural volume in these samples; this is the characteristics of their glassy nature.

Figure 3a shows the DSC plots of the synthesized glass samples. The glass transition temperature of the samples decreases with increase in ZnCl\(_2\) content which indicates progressive increase in the concentration of the non-bridging oxygen (NBO) atoms.\(^{29, 30}\) The glass transition temperature (\(T_g\)) has been estimated from the minima occurred in the graph of \(dH/dT\) versus temperature. A typical plot of \(dH/dT\) versus temperature for glass sample with

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<th>(x = 15)</th>
<th>(x = 20)</th>
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<td>(V_m) (m(^3).mol(^{-1})) \times 10^{-6}</td>
<td>30.938</td>
<td>32.052</td>
<td>32.791</td>
<td>33.296</td>
<td>35.607</td>
</tr>
<tr>
<td>(V_c) (m(^3).mol(^{-1})) \times 10^{-6}</td>
<td>30.672</td>
<td>31.291</td>
<td>31.910</td>
<td>32.530</td>
<td>33.149</td>
</tr>
<tr>
<td>(T_g) (°C)</td>
<td>347</td>
<td>340</td>
<td>329</td>
<td>317</td>
<td>308</td>
</tr>
<tr>
<td>(E_g) (eV)</td>
<td>3.31</td>
<td>3.42</td>
<td>3.46</td>
<td>3.49</td>
<td>3.52</td>
</tr>
<tr>
<td>(\lambda_c) (nm)</td>
<td>375</td>
<td>363</td>
<td>358</td>
<td>355</td>
<td>352</td>
</tr>
<tr>
<td>(n)</td>
<td>2.318</td>
<td>2.292</td>
<td>2.283</td>
<td>2.276</td>
<td>2.269</td>
</tr>
<tr>
<td>(R_m) (m(^3)) \times 10^{-6}</td>
<td>17.891</td>
<td>18.798</td>
<td>19.153</td>
<td>19.388</td>
<td>20.670</td>
</tr>
<tr>
<td>(M)</td>
<td>0.406</td>
<td>0.413</td>
<td>0.416</td>
<td>0.418</td>
<td>0.419</td>
</tr>
<tr>
<td>(\Delta E) (eV)</td>
<td>0.21</td>
<td>0.25</td>
<td>0.26</td>
<td>0.30</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Fig. 2 – Variation of molar volume (\(V_m\)) and crystalline volume (\(V_c\)) with ZnCl\(_2\) concentration (mol%).

Fig. 3 – (a) DSC plots of the synthesized glass samples, (b) \(dH/dT\) curve for glass sample containing 10 mol% ZnCl\(_2\).
$x = 10$ is shown in Fig. 3b. The decrease in the $T_g$ implies a decrease in the rigidity of the tellurite glass network.\textsuperscript{31}

The study of optical absorption, particularly the absorption edge, is a useful method for investigation of optical transitions as well as estimating energy gap and band structure of both crystalline and non-crystalline materials. Figure 4 shows the optical absorption spectra of the glass samples under investigation. The cut off wavelength ($\lambda_c$) and the optical band gap energy ($E_{opt}$) of the glass samples have been calculated from the UV-Vis absorption spectrum. On addition of zinc chloride the position of the fundamental absorption edge and cut off wavelength shifts towards the lower wavelength side. This shifting is due to progressive increase in the number of bridging oxygen (BO) atoms as the bridging oxygens are more excited than NBO's.\textsuperscript{31}

![Optical absorption spectra as a function of wavelength of the glass samples](image)

The optical absorption coefficient $\alpha(h\nu)$ and the optical band gap energy $E_{opt}$ in many amorphous materials are related as:\textsuperscript{32}

$$\alpha(h\nu) = A(h\nu - E_{opt})^m$$  \hspace{1cm} (2)

where $h\nu$ is the incident photon energy, $A$ is a constant and the exponent $m$ is a parameter which depends on the type of electronic transition responsible for absorption. It has different values: $1/2$, $2$, $1/3$ and $3$ corresponding to direct allowed, indirect allowed, direct forbidden and indirect forbidden transitions respectively. Tauc’s plots, i.e. change in $(\alpha(h\nu))^{1/m}$ on $h\nu$, for different values of $m$ ($1/2$, $2$, $1/3$ and $3$) have been studied. The plots for $m = 1/2$ have been found to be most suitable and is shown in Fig. 5. Lower energy region in the Tauc’s plot is shown just for sake of clarity. Various researchers have also shown the same type of plots.\textsuperscript{24, 28, 33, 34} Thus, the present glass system shows direct allowed transitions. The optical band gap energies of different glass samples are estimated by extrapolation of the linear region curve to meet $h\nu$ axis, i.e. $(\alpha(h\nu))^2 = 0$, and the values are listed in Table I.

![Tauc’s plots for different glass samples for $m = 1/2$](image)

In the present glass system there is appreciable increase in the $E_{opt}$ on addition of ZnCl$_2$. The large optical band gap energy provides a possibility that glass may be applicable in the optical device components.\textsuperscript{35}

Urbach energy is used to characterize the degree of the disorderliness in amorphous and crystalline solids, which can be estimated using the Urbach equation:\textsuperscript{36}

$$\alpha(h\nu) = B \exp(h\nu/\Delta E)$$  \hspace{1cm} (3)

where $B$ is constant and $\Delta E$ is the width of the band tail of the electron states. Equation (3) can be rewritten as:

$$\ln \alpha(h\nu) = h\nu/\Delta E + \text{constant}$$  \hspace{1cm} (4)

$\Delta E$ can tell us about the defect concentration as materials with high Urbach energy would have greater tendency to convert Te-O weak bonds into defects.\textsuperscript{37, 38} The Urbach energy was determined from the slope of the linear region of the curve $\ln(\alpha)$ versus $h\nu$ (Fig. 6). The values of $\Delta E$ (listed in Table I) lie in the range of 0.21-0.33, which correspond to amorphous semiconductors as reported by Mott and Davis.\textsuperscript{39} The lower value of Urbach energy suggests that the defects in these glass samples are minimum.\textsuperscript{40} The increase in Urbach energy values with
increase in ZnCl$_2$ concentration indicates conversion of large number of weak bonds into defects. The same is also supported by the decrease in glass transition temperature ($T_g$) and molar volume, and increase in the optical band gap ($E_{opt}$).

Refractive index ($n$) is determined from the optical band gap energy ($E_{opt}$) using the relation proposed by Dimitrov and Sakka: $^{41}$

\[
\frac{(n^2-1)}{(n^2+2)} = 1 - \frac{1}{(E_{opt}/20)} \quad \text{..(5)}
\]

The molar refractivity ($R_m$) has been calculated by using the relation: $^{42}$

\[
V_m\left[\frac{(n^2-1)}{(n^2+2)}\right] = R_m \quad \text{..(6)}
\]

The values of the refractive index and molar refractivity are presented in Table I. It can be observed that the refractive index decreases and molar refractivity increases with increase in ZnCl$_2$ content. The changes in the refractive index can result from a number of factors such as fluctuation of glass composition, inhomogeneity in the sample, polarization ability of the glass constituent ions, etc. In case of polarization of the ion introduced into glass, generally, the refractive index of the glass increases with the polarizability of the ion. As the polarizability of ZnCl$_2$ is lower than that of BaO, a decrease in the refractive index is expected with the increase in ZnCl$_2$ content in the glass. In addition, since the refractive index of a glass is also related to its density, the lowering of the glass density induced by the introduction of ZnCl$_2$ will also contribute to the decrease in refractive index. $^{43}$

The metallization criterion ($M$) of an oxide on the basis of its linear refractive index or energy band gap is given by: $^{44}$

\[
M = 1 - R_m/V_m \quad \text{..(7)}
\]

Table I shows the values of the metallization criterion of the prepared glasses. Oxide glasses with good non linear optical properties possess a metallization criterion of approximately 0.35-0.45. It has also been observed that the studied glass samples possess a metallization criterion in the range of 0.406-0.417 (Table I). This suggests the materials under investigation to be new non linear optical materials having applications in optical modulators, memories, optical switches and limiters, optical computers, optoelectronics, controlling beam breakup in high power lasers and non linear spectroscopy. $^{45-47}$

Conclusions

Glass samples of the studied composition 70TeO$_2$-(30-\(\chi\))BaO-xZnCl$_2$ have been successfully synthesized by rapid melt quenching technique. Glassy nature of the prepared samples has been ascertained by X-ray diffraction pattern. It has been observed that:

i. The molar volume was higher than the crystalline volume, which proves the amorphous nature of the prepared glass samples.

ii. The glass transition temperature decreased with increase in ZnCl$_2$ concentration.

iii. The Urbach energy increased with increase in ZnCl$_2$ content.

iv. Direct allowed transitions are most probable in the system of present study and the optical band gap energy ($E_g$) was calculated from the Tauc's plot.

v. Refractive index decreased and molar refractivity increased with increase in ZnCl$_2$ content.

vi. The Urbach energy increased with increase in the ZnCl$_2$ content, which indicates that the defect concentration was minimum.

Metallization criterion of these glass samples shows the suitability for new non linear optical materials.

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References

Electronic transport and relaxation studies in bismuth modified zinc boro-tellurite glasses

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A B S T R A C T

The ac conductivity of tellurium based quaternary glasses having composition 60 TeO2 – 10 ZnO – (30 – x) Bi2O3 – xB2O3; x = 0, 5, 10, 15 and 20 has been investigated in the frequency range 10−3 Hz to 105 Hz and in the temperature range 483 K–593 K. The frequency and temperature dependent ac conductivity increase with increase in bismuth content and found to obey Jonscher’s universal power law. The dc conductivity, crossover frequency and frequency exponent have been estimated from the fitting of the experimental data of conductivity with Jonscher’s universal power law. In the studied glasses the ac conduction may be described by overlapping of large polaron tunneling model. The activation energy is found to be decrease with increase in bismuth content and variable range hopping (VRH) proposed by Mott with some modification suggested by Punia et al. is more or less suitable to explain dc conduction. The value of the stretched exponent (β) obtained by fitting of M0 reveals the presence of non-Debye type of relaxation in the presently studied glass samples. Scaling spectra of electric modulus (M’ and M”) collapse into a single master curve for all the compositions and temperatures. The values of activation energy of electric modulus (Ea) and conduction (W) are nearly equal for all the studied glasses, indicating that the polaron have to overcome the same energy barrier during conduction as well as relaxation processes. The conduction and relaxation process in the presently studied glass samples are composition and temperature independent.

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1. Introduction

Heavy metal oxide glasses such as TeO2, Bi2O3 etc. have been studied extensively in the recent years [1–4] due to their wide applications in the field of glass ceramics, layers for optical and electronic devices, thermal and mechanical sensors, reflecting windows, etc. [5–9]. TeO2 based glasses have low melting temperatures, high dielectric constant, and good infra red transmissions [10–13], which makes them suitable candidates for a wide range of applications such as optical materials used in laser technology [14,15] and fast-ions conducting solid electrolytes [16,17]. Glasses containing Bi2O3 and ZnO have a long infra red cut off and third order non linear optical susceptibility which make them ideal candidate for application as infra red transmission components and photonic devices [18,19]. Addition of heavy metal oxides (like Bi2O3, Nb2O3) to tellurite glasses enhances both the physical and optical properties of these glasses and addition of ZnO to tellurite glass network increases the stability of glass network and glass forming ability [20,21]. The temperature dependence of conductivity of tellurite glasses has been found to show the characteristic transition between conduction in a polaron band and due to hopping [22,23]. The conductivity in these glasses depends on number of mobile charge carriers and their mobility [24]. The electronic transport properties of TeO2 – Bi2O3, TeO2 – V2O5 – Bi2O3, TeO2 – ZnO, Bi2O3 – B2O3 – ZnO and other tellurite based glass system have been studied by many researchers [25–30]. But, there is hardly any report in literature on systematically composition and frequency dependent ac conductivity, scaling behavior, electric modulus formulation and conduction mechanism of TeO2 – Bi2O3 – B2O3 – ZnO glass system.

In the present study, we report the ac conductivity, dielectric...
2. Experimental

Glasses having compositions 60 TeO₂ − 10ZnO − (30 − x) B₂O₃ − xBi₂O₃; x = 0, 5, 10, 15 and 20 were prepared using analar grade ZnO, B₂O₃, B₂O₃ and TeO₂ chemicals by melt-quench technique. The detailed discussion of preparation of studied glass system is reported elsewhere [1]. X-ray diffraction studies of the samples performed using Rigaku Table-Top X-Ray Diffractometer confirm the amorphous nature of these samples. The values of glass transition temperature (Tₙ) of different samples were measured by DSC technique using TA Instruments, Model no. Q600 SDT, at a heating rate 10°C/min in nitrogen atmosphere. The glass samples were cut and ground to get rectangular shapes with thickness about 1 mm and their surfaces were polished. For electrical measurements, both sides of the polished samples were coated with silver to serve as electrodes. Conductivity measurements were carried out by using Alpha-A high resolution dielectric, conductivity, impedance, and gain phase modular measurement system by Novocontrol Technologies GmbH & Co. KG in the frequency range of 10⁻¹ Hz to 10⁵ Hz and temperature ranging from 483 K to 593 K. The fitting of experimental data was done by using linear fit and non-linear curve fitting modules of Origin Pro 8.6 software.

3. Results and discussion

The ac conductivity of different glass compositions of 60 TeO₂ − 10ZnO − (30 − x) B₂O₃ − xBi₂O₃; x = 0, 5, 10, 15 and 20 glass system recorded in temperature range 483 K–593 K and frequency range 10⁻¹ Hz to 10⁵ Hz show similar frequency and temperature dependence. The frequency dependent conductivity goes on increasing with increase Bi₂O₃ content in studied frequency range at any particular temperature, a typical compositional variation of σ’(ω) with frequency at 553 K is shown in Fig. 1.

The frequency dependent conductivity is characterized by two regions: (i) plateau region and (ii) dispersion region as observed for various other oxide glasses [24–28].

The ac conductivity σ’(ω) of the studied glass system is analyzed in the light of Jonscher’s Universal Power Law [31,32],

\[ \sigma'(\omega) = \sigma_{dc} \left[ 1 + \left( \frac{\omega}{\nu_H} \right)^s \right] \]  \hspace{1cm} (1)

where \( \sigma_{dc} \) is direct current (dc) conductivity, \( \nu_H \) is crossover frequency separating dc regime (plateau region) from the dispersive conduction and s is frequency exponent that lies between 0.7 and 1 [31,33]. The values of \( \sigma_{dc}, \nu_H \) and s are obtained by the fitting of the experimental data of \( \sigma'(\omega) \) measured at different temperatures with Eq. (1). As shown in Fig. 2, the experimental data fitted with Jonscher’s universal power law (Eq. (1)) gives very good fitting with best parameter fit, \( R^2 \), in the range 0.9995–0.9998. Jonscher’s universal power law is observed to be obeyed in all the presently studied glass compositions indicating that the ac conduction in the present glass system may be attributed to hopping mechanism [31].

The conduction mechanism in any material could be understood from the temperature dependent behavior of frequency exponent (s). Various models based on classical hopping of charge carriers over barrier, quantum mechanical tunneling and the overlapping large-polaron tunneling [24,34–39], have been proposed on the basis of variation of frequency exponent with temperature and frequency.

(i) If s decreases with temperature then it follows correlated barrier hopping (CBH) conduction mechanism [40].

(ii) If s depends upon frequency but is independent of temperature then the conduction mechanism can be explained by the quantum mechanical electron tunneling theory [40].

(iii) If s increases with increase in temperature, then the conduction process can be explained with the small polaron quantum mechanical tunneling theory where as if s decreases at first, reaching a minimum and increases thereafter with increase temperature then it can be explained by large polaron quantum mechanical tunneling model [40].

The temperature dependence of frequency exponent (s) obtained from the fitting of experimental data with Eq. (1) is found to be lying between 0.7 and 1 in the studied range of temperature. For the presently studied glass system, frequency dependence of s has not been observed in the studied frequency range, so temperature dependence of frequency exponent plays a key role in estimation of conduction mechanism. In studied tellurium based quaternary glasses, s first decreases and attains minima and then after, it.

![Fig. 1. Compositional variation of total ac conductivity \( \sigma'(\omega) \) of 60 TeO₂ − 10ZnO − (30 − x) B₂O₃ − xBi₂O₃ glass composition at 553 K.](image_url)

![Fig. 2. Measured total ac conductivity \( \sigma'(\omega) \) for 60 TeO₂ − 10ZnO − (30 − x) B₂O₃ − xBi₂O₃ glass composition shown as function at twelve different temperatures. The solid lines in the figure are the best fits obtained from fitting of experimental data with Jonscher’s power law.](image_url)
increases with temperature as shown in Fig. 3. So, the conduction mechanism in the studied glass system may be attributed to Overlapping Large Polaron Tunneling (OLPT).

The mechanism of charge carriers transport has also been studied using the reduced plot of frequency versus reduced conductivity. In the past few years different scaling models have been proposed. The ac conductivity of the studied glass system has been scaled by $\sigma_{ac}$, while the frequency axis is scaled with Jonscher’s cross-over frequency ($\omega_H$) as scaling frequency. It has been observed that both compositional and temperature dependent scaling spectra lie on a single master curve confirming that $\omega_H$ is appropriate scaling frequency and all the studied glass compositions have similar conduction mechanism. A typical plot of scaling spectra at different temperatures for $x = 5$ and different compositions at a particular temperature at 523 K is shown in Figs. 4 and 5 respectively. The results of ac scaling are in accordance with those obtained from study of frequency exponent i.e. all the glass compositions shows similar type of conduction mechanism in the studied frequency and temperature range.

DC conductivity has been obtained from fitting of the experimental data of $\sigma^2 (\omega)$ at different temperatures with Jonscher’s equation and it is observed that it lies in the range from $10^{-10}$ to $10^{-6}$ S cm$^{-1}$. As shown in Fig. 6, the dc conductivity is observed to obey Arrhenius behavior, expressed by the following equation [40,41]:

$$\sigma_{dc} (T) = \sigma_o \exp \left[ -W/kT \right] \tag{2}$$

where $\sigma_o$ is the pre-exponential parameter which depends on the semiconductor nature, $W$ denotes the thermal activation energy of electrical conduction and $k$ is Boltzmann constant. The activation energy ($W$) values have been calculated from the slope of log $\sigma_{dc}$ versus 1000/T graph obtained from linear fitting of the experimental data. The values of $W$ have been listed in Table 1. The activation energy is observed to decrease indicating thereby increase in conductivity with increase in bismuth content. It may be due to increase in the number of non-bridging oxygen (NBOs) with increase in bismuth content in the studied glass system [25,42]. The increase in NBOs facilitates the easy movement of charge carriers in the glass network. Differential Scanning Calorimetry (DSC), Fourier Transform Infrared spectroscopy (FTIR) and Raman spectroscopy also reveals the increase in NBOs on addition of Bi$_2$O$_3$ in the studied system [1]. The decrease in activation energy is found to be
consistent with decrease in the band gap energy on increasing bismuth [1].

The concentration of bismuth ions (N) has been estimated using the following relation [43]:

\[ N = 2dN_A \frac{W_{Bi_2O_3}}{MBi_2O_3} \]  (3)

where \( d \) is the density, \( MBi_2O_3 \) is molecular weight of \( Bi_2O_3 \), \( W_{Bi_2O_3} \) is weight fraction of \( Bi_2O_3 \) and \( N_A \) is the Avogadro’s number. The correlation between \( N \) and mean spacing between any two \( Bi^- \) ions (\( R \)) is generally described as [43,44].

\[ R = \left( \frac{1}{N} \right)^{\frac{1}{3}} \]  (4)

Using above relations, polaron radius (\( r_P \)) is given by [43,45].

\[ r_P = \frac{1}{2} \left( \frac{\pi}{6} \right)^{\frac{1}{3}} R \]  (5)

The density of states, \( N(E_F) \) for the thermally activated electron hopping near the Fermi level is calculated by the relation [38,43]:

\[ N(E_F) = \frac{3}{4\pi R^3 W} \]  (6)

The values are of the order of \( 10^{20} \) eV \(^{-1} \) cm \(^{-1} \) and the calculated values of \( W, N, R, r_P \) and \( N(E_F) \) are given in Table 1 shows that activation energy decrease with increase in conductivity, which is an expected result and is attributed to decrease in the polaron hopping distance, \( R \) with increase in bismuth content.

A variable range hopping (VRH) conduction given by Mott in low temperature range with some modification suggested by Punia et al. in intermediate temperature region (\( Bo = 6.8 \)) is used to explain three dimensional VRH in bulk disordered semiconductors. The plot \( \log \sigma_{dc} \) versus \( T^{-1/4} \) (shown in Fig. 7) gives better linear fit with linearity \( -0.9999 \) in comparison to the Arrhenius plots i.e. \( \log \sigma_{dc} \) versus \( 1000/T \) which shows linearity \( -0.999 \). So, VRH model is suitable for describing the dc conductivity in the studied glass samples. The dc conductivity for 3-D Mott VRH model with modifications described by Punia et al. [43,46].

\[ \sigma_{dc} = A e^{\left[ \frac{W}{kN(\ E_F)} \right]} \]  (7)

where \( A \) and \( B \) are constants, given by relations

\[ A = \nu_{ph} e^2 N(E_F) R^2 \]  (8)

\[ B = B_0 \left[ \frac{e^3}{kN(\ E_F)} \right]^4 \]  (9)

where \( \alpha \) is the inverse localization length of s-like wave function. \( B_0 \) is a constant taken as 6.8 [43]. The values of \( \alpha \) are tabulated in Table 1 are in very good agreement with those suggested by Murawski et al. [47] for oxide glasses. The values of \( \alpha R \) are comparable to one (3.41–3.45) in the studied glass samples. So, VRH conduction may be applicable to the present glass system. The inequality \( \alpha < r_P < R \) is satisfied in the whole temperature range, so the polaron theory is applicable in the presently studied glass compositions.

In terms of complex dielectric constant (\( e^* \)), the complex electric modulus is defined as [48,49].

\[ M^* = (e^*)^{-1} \]  (10)

and

\[ M^* = M' + iM'' = \frac{\varepsilon'}{\varepsilon''^2 + (\varepsilon')^2} + i \frac{\varepsilon''}{\varepsilon''^2 + (\varepsilon')^2} \]  (11)

where \( M', M'' \) and \( \varepsilon', \varepsilon'' \) are the real and imaginary parts of the electric modulus and dielectric constants, respectively. The real part of modulus spectrum at different temperatures shows the general trend as shown by various other semiconducting glasses [25,50,51]. I.e. at lower frequencies it appears to zero while at higher
frequencies a plateau is obtained. A typical graph of $M'$ spectrum at different temperature is shown in Fig. 8. The negligible value of $M'$ at lower frequencies indicates that the electrode polarization have a negligible contribution to $M'$ and the dispersion is mainly due to conductivity relaxation \[52-54\], while at higher frequencies, $M'$ reaches a maximum constant value $M_\infty$. The value of $M_\infty$ decreases with the increase in temperature, this decrease in $M_\infty$ may be due to bismuth content \[25\].

The imaginary part of electric modulus for $x = 5$ sample as a function of frequency at various temperatures is shown in Fig. 9. The plot exhibit a clear relaxation peaks at characteristics frequencies and peak is found to shift to higher frequencies with increasing and temperature. The appearance of peaks in the modulus spectra is clear indication of the conductivity relaxation process. The peak represents that there is changeover in mobility of polaron from long range to short range. The polaron have the capability to move long distance below the frequency region where peak occurs but the polaron are restricted to move only within potential well above the frequency range \[25,26,51\].

The imaginary part of electric modulus ($M_0^*$) could be expressed as Fourier transform of a relaxation function $\Phi(t)$ \[51,53\].

\[
M^* = M_\infty \left[ 1 - \int_0^\infty \exp(-\omega t) \left( \frac{d\Phi}{dr} \right) dr \right]
\]  
\[\text{(12)}\]

where $M_\infty$ is the high-frequency asymptotic value of real part of the dielectric constant and the function $\Phi(t)$ is the time evolution of the electric field within the material and usually taken as the Kohlrausch–Williams–Watts (KWW) function \[55,56\].

\[
\Phi(t) = \exp \left[ - \frac{t}{\tau_M} \right]^{\beta}
\]  
\[\text{(13)}\]

where $\tau_M$ is the conductivity relaxation time and the term $\beta$ is the stretched exponent and is a measure of the degree of interaction between the charge carriers. The value of $\beta$ varies in between 0 and 1 and for an ideal Debye-type relaxation the value of $\beta$ equals to 1 \[25\]. The values of $\beta$ can be calculated based on electric modulus studies carried out at various temperatures. The electric modulus behavior of presently studied glass system is analyzed by the modified KWW function as suggested by Bergman \[57\]. Accordingly, the imaginary part of electric modulus may be represented as

\[
M^* = \frac{M_{\text{max}}^*}{\left( 1 - \beta \right)} + \frac{\beta}{T_{\text{max}}} \left[ \frac{f}{f_{\text{max}}} \right]^\beta
\]  
\[\text{(14)}\]

where $M_{\text{max}}^*$ is the peak value of $M^*$ and $f_{\text{max}}$ is the corresponding frequency. The value of $M_{\text{max}}^*$, $f_{\text{max}}$ and $\beta$ are determined from the linear fitting of the experimental data of $M^*$ gives very good fitting with best parameter fit, $R^2$, in the range 0.9995–0.9998. It is observed that with increase in bismuth content, the value of peak frequency ($f_{\text{max}}$) increases. The values of $\beta$, obtained from fitting, are presented in Fig. 10 and they are lying in between 0.73 and 0.84. Perusal of the data presented in Fig. 11, it is observed that $\beta$ has a very small temperature dependency suggesting a non-Debye type relaxation mechanism \[58\].

The relaxation time $\tau_M$ has been calculated by the relation

\[
\tau_M = \frac{1}{2\pi f_{\text{max}}}
\]  
\[\text{(15)}\]
and it is found to lie in the range 1.14 ms–718 μs. The relaxation time shows a decreasing trend with increase in bismuth content (relaxation times of various compositions at 553 K are presented in Table 1). This is in accordance with the results of conductivity as the conductivity of the present glass system also increases with increase in bismuth content. The activation energy involved in the relaxation process could be obtained from the temperature dependent relaxation time as

\[
\tau_M = \tau_0 \exp \left( \frac{E_R}{kT} \right)
\]

\[(16)\]

where \(E_R\) is the activation energy associated with the relaxation process or modulus relaxation energy, \(\tau_0\) is pre exponential factor, \(k\) is Boltzmann constant, and \(T\) is absolute temperature. The linear fitting of plots between \(\log \tau_M\) and \(1/T\) for different compositions of the presently studied glass system is shown in Fig. 11. The estimated values of activation energy are presented in Table 1. Perusal of the data presented in Table 1, shows that both the dc activation energy (W) and the modulus relaxation energy (E_R) shows the same trend i.e. both show a decrease in their values with increase in bismuth content (x). Perusal of data presented in Table 1, it is observed that the values of \(E_R\) and W are nearly equal for all the studied compositions, suggesting that the polaron have to overcome the same energy barrier during conduction as well as relaxation processes.

The reduced part of the electric modulus (\(M'/M'_\infty\) and \(M''/M''_{\max}\)) has been plotted as a function of reduced frequency (\(f/f_{\max}\)) for different glass compositions and different temperatures shown in Figs. 12 and 13. The modulus spectra for both compositions and temperatures overlap on a single master curve indicates that relaxation process in the presently studied glass samples are composition and temperature independent [50].

4. Conclusions

The ac conductivity of tellurium based quaternary glasses has been investigated in the frequency range \(10^{-1}\) Hz to \(10^3\) Hz in the temperature range 483 K–593 K and is found to be increase with increase in bismuth content. The observed dispersion behavior of ac conductivity of tellurium based quaternary glasses obeys the Jonscher’s universal power law and the theoretical fitting of experimental data for Jonscher’s power law is in good agreement for all compositions. Further it is observed that the Overlapping Large Polarons Tunneling (OLPT) Model is more or less suitable to describe the ac conduction mechanism of present glass system. The activation energy for dc conduction is found to be decrease with increase in bismuth content and dc conduction takes place via variable range hopping (VRH). The imaginary part of modulus (\(M''\)) spectra has been fitted to modified Kohlrausch-Williams-Watts (KWW) function. The value of the stretched exponent (\(β\)) reveals the presence of non-Debye type of relaxation in the presently studied glass samples. Scaling spectra of electric modulus (\(M'/M'_\infty\) and \(M''/M''_{\max}\)) versus \(f/f_{\max}\) for \(x = 10\) at different temperatures.