Dielectric dispersion in ZnF_2-Bi_2O_3-TeO_2 glass system

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Dielectric constant ε', loss $\tan\delta$ and ac conductivity σ of ZnF_2-Bi_2O_3-TeO_2 glasses with varying concentrations of Bi_2O_3 (from 5 to 20%) are studied as a function of frequency and temperature over moderately wide ranges. The dielectric breakdown strength for these glasses is also determined in air medium. From the analysis of these studies along with the IR spectra & DTA recordings of these glasses, the structural changes in ZnF_2-Bi_2O_3-TeO_2 glass system with change in the concentration of Bi_2O_3, are discussed.
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1. Introduction

TeO_2 based glasses, especially ZnF_2-MO-TeO_2 systems (where MO stands for modifier oxide) are well known due to their high transparency in the far infrared region and for their high density and refractive index. These glasses are very stable against devitrification, nontoxic and are resistant to moisture. In view of these qualities these glasses were considered as the best materials for optical components such as IR domes, optical filters, modulators, memories and laser windows.

Recently we have reported numerous studies on mechanical, electrical and optical properties of tellurite glasses containing different rare earth ions with PbO as modifier [1, 2]. These studies have yielded valuable information regarding the mechanical and insulating strengths and threw some light on the possible use of these glasses as host material for laser emission. Damarawi has recently reported in detail the modifier action of PbO and PbF_2 in TeO_2 glass network and also electrical behaviour and mixed mobile ion (Na^+ and Ag^+) effects in some tellurite glass systems [3–5]. However in recent years, it has been observed that, these TeO_2 based glasses exhibit semi-conducting behaviour when the conventional modifiers like PbO are replaced with other heavy metal oxides like Sb_2O_3, Mo_2O_3, Fe_2O_3, Bi_2O_3 etc., [6–9] in these systems. The heavy metal ions such as bismuth ions dissolved in tellurite glass matrix, influence the insulating character of these glasses very strongly; these ions have high polarisability and are expected to play dual role, one as modifier with BiO_6 (octahedral) and the other as glass former with BiO_3 (pyramidal) structural units. The content of different structural units of bismuth oxide, at a given temperature in these glasses depends on the quantitative properties of other modifiers and glass formers, the size of the ions in the glass structure, their field strengths and composition of the glass etc. Hence the connection between the position of bismuth ion in volatile TeO_2 glass network and the electrical properties of these

glasses is expected to be quite interesting. Though considerable studies on electrical properties along with optical properties [10, 11] of some TeO_2 based glasses are available in literature, majority of these studies are devoted to binary tellurite glasses and further they are mainly concentrated on dc conductivity studies [12–14]. Much devoted studies on electrical properties, especially on dielectric relaxation, ac conductivity and dielectric breakdown strength on particularly interesting ZnF_2-Bi_2O_3-TeO_2 (interesting because it combines a partially fluorinated compound together with tellurite and heavy metal oxide) system are not available. Knowledge on these properties is highly helpful for estimating insulating strength of these glasses and may also pave way for the analysis of the structure of this glass system to some extent.

In our earlier paper, the structural role of P_2O_5 in ZnF_2-TeO_2 glass system has been reported [15]. The present investigation is undertaken to have a comprehensive understanding over the influence of bismuth ions on the insulating character of ZnF_2-Bi_2O_3-TeO_2 glasses, from a systematic study on dielectric constant (ε'), loss ($\tan\delta$), ac conductivity (σ) in the frequency range 10^2–10^5 Hz and in the temperature range 30–200°C and also dielectric breakdown strength in air medium along with infrared spectra and DTA; and it is further aimed at an understanding the structure of this glass system by using the results of these studies.

2. Experimental methods

Within the glass forming region of the ZnF_2-Bi_2O_3-TeO_2 glass system (Fig. 1), the following five particular compositions with successive increase in the concentrations of Bi_2O_3 are chosen for the present study:

Glass A: 40 ZnF_2-05 Bi_2O_3-55 TeO_2
Glass B: 40 ZnF_2-10 Bi_2O_3-50 TeO_2
Glass C: 40 ZnF_2-12 Bi_2O_3-48 TeO_2
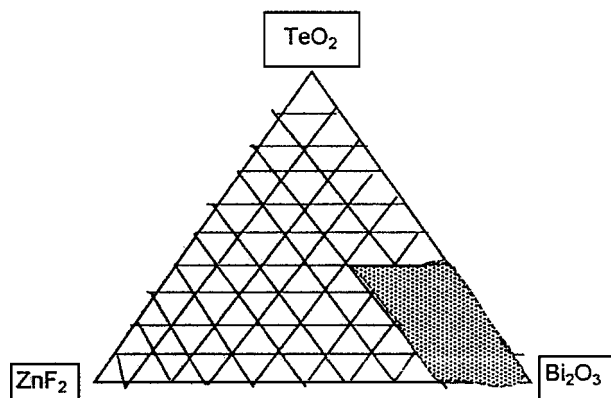
Figure 1 Approximate glass forming region ZnF_2-Bi_2O_3-TeO_2 glasses.

Glass D: 40 ZnF_2-15 Bi_2O_3-45 TeO_2
Glass E: 40 ZnF_2-20 Bi_2O_3-40 TeO_2.

However, it may be noted here, that clear glass was not formed when concentration of Bi_2O_3 was increased beyond 20% in this series (Fig. 1).

Appropriate amounts (all by wt%) of reagent grade TeO_2 (99.99% pure, Aldrich), Bi_2O_3 (99.99% pure, Loba) and ZnF_2 (99.99% pure, Loba) were thoroughly mixed in an agate mortar and melted in a platinum crucible between 700–750°C in a PID temperature controlled furnace for about 1/2 h until a bubble free liquid was formed. The resultant melt was then cast in a brass mould and subsequently annealed at 200°C. The amorphous state of the glasses was checked by X-ray diffraction spectra; it is further confirmed by pictures taken using JEOL JSM-T330A Scanning Electron Microscope. Samples were ground and polished to a thickness of ~0.2 cm and were ~1 cm x 1 cm in area. Silver paint applied to the faces of the sample served as electrodes for the dielectric measurements. An LCR bridge (Hewlett Packard Model-4263 B) was used to carry out the dielectric measurements. It may be mentioned here that the dielectric measurements were repeated for some of these samples with gold coating and the results obtained were almost identical with those of the silver painted samples. The accuracy in the measurement of dielectric constant ε' is ~±0.001 and that in dielectric loss $\tan\delta$ is ~10^{-4}. Dielectric breakdown strength for all the glasses was determined at room temperature in air medium using a high ac voltage breakdown tester (ITL Model AAH-55, Hyderabad) operated with an input voltage of 250 V of frequency 50 Hz; it was ensured that all the glasses used for this study were almost of equal thickness. The IR transmission spectra were recorded using a BRUKER IFS 66v, FT-IR spectrometer. The differential thermal analysis of these samples is carried out in air with a SEIKO TG/DTA 32 balance with a programmed heating rate of 20°C per minute in the temperature range 30–1000°C.

3. Results
The variation of the glass transition temperature T_g (evaluated from differential thermal analysis) with Bi_2O_3 concentration exhibited a downward kink at about 12% of Bi_2O_3 (Fig. 2). The same figure also presents the variation of parameters T_g/T_m, $(T_c - T_g)/T_g$,
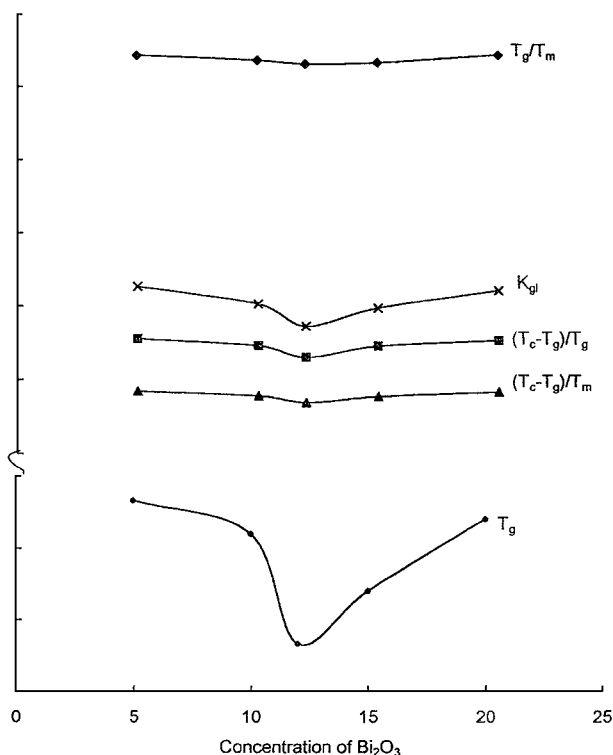

Figure 2 Variation of K_{gl}, $(T_c - T_g)/T_g$, $(T_c - T_g)/T_m$, T_g/T_m and T_g with Bi_2O_3 concentration in ZnF_2-Bi_2O_3-TeO_2 glasses.

$(T_c - T_g)/T_m$ and $K_{gl} = (T_c - T_g)/(T_m - T_c)$ [where T_c is the crystallization temperature and T_m indicates the temperature of re-melting] with the concentration of Bi_2O_3.

The dielectric constant ε' at room temperature of glass A (containing 5% of Bi_2O_3) at 10^5 Hz is measured to be 11.62; the dielectric constant ε' and loss $\tan\delta$ are found to increase slightly with decrease in frequency for all the glasses; however the room temperature values of ε' and $\tan\delta$ at a fixed frequency are found to increase with increase in the concentration of Bi_2O_3 up to 12%, beyond that these values are found to decrease (Fig. 3).

The temperature dependence of ε' for these glasses measured at a frequency of 1 kHz is shown in Fig. 4; ε' is found to increase at higher temperatures. In addition it is also observed that the value of ε' (at a fixed temperature & frequency) increased with increase in concentration of Bi_2O_3 up to 12% and further increase in Bi_2O_3 concentration led to a decrease in these values.

The variation of dielectric loss $\tan\delta$ of ZnF_2-Bi_2O_3-TeO_2 glasses with temperature at different frequencies has exhibited distinct maxima; with increasing frequency, the temperature maximum shifted towards higher temperatures and with increasing temperature the frequency maximum shifted towards higher frequencies, indicating dipolar relaxation character of dielectric loss in these glasses. Fig. 5 shows such a behavior of $\tan\delta$ for glass C (containing 12% of Bi_2O_3). As mentioned in the experimental methods, results of the measurements on gold coated samples have also exhibited relaxation phenomenon at about same temperature regions in these glasses; this indicates the observed relaxation phenomenon is a characteristic of these glasses and not due to any electrode effects.
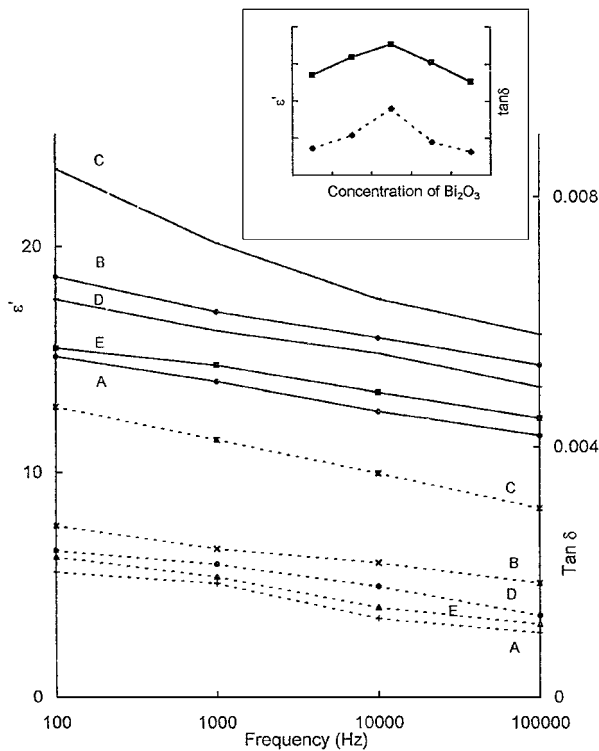
Figure 3 Variation of dielectric constant (solid lines) and dielectric loss (dotted lines) with frequency at room temperature for ZnF$_2$-Bi$_2$O$_3$-TeO$_2$ glasses (Inset gives the variation of ε' and tan δ with concentration at 10 K).

The effect of Bi$_2$O$_3$ content on the relaxation strength of these glasses can clearly be understood from Fig. 6 in which tan δ is plotted against temperature at 100 kHz for all these glasses; it isobserved that the relaxation peak
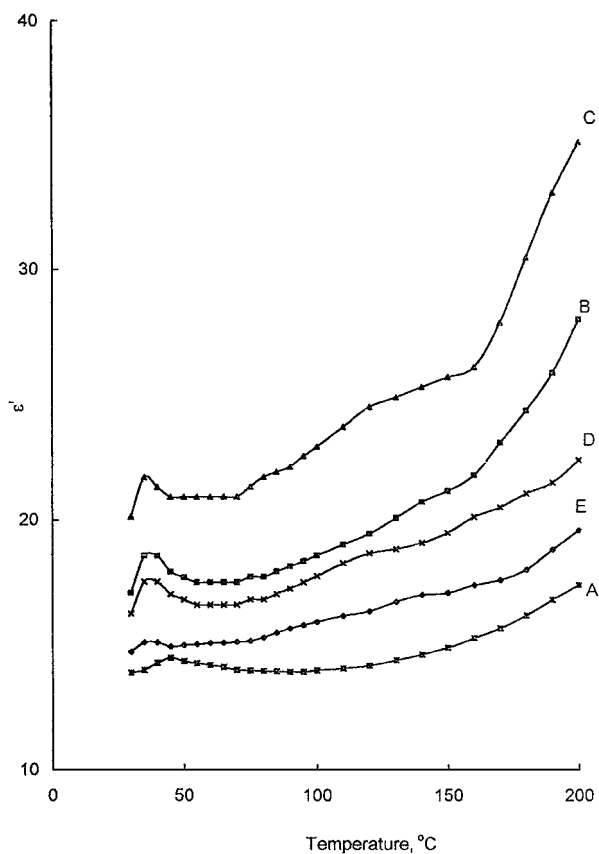

Figure 4 Variation of dielectric constant with temperature for ZnF$_2$-Bi$_2$O$_3$-TeO$_2$ glasses at 1 kHz.
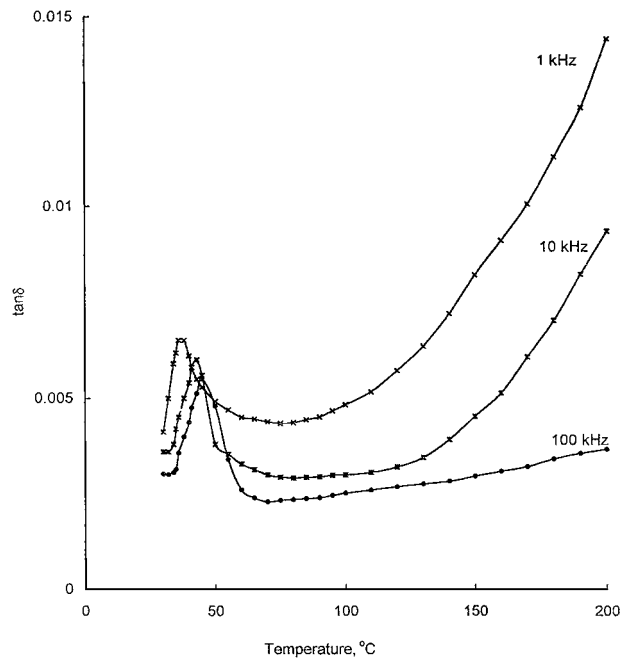

Figure 5 Variation of dielectric loss with temperature at different frequencies for glass C.

has broadened and shifted towards lower temperatures (with ascending values of (tan δ)$_{max}$) with increase in Bi$_2$O$_3$ concentration up to 12%, beyond this concentration the relaxation peaks are found to become narrow (with descending values of (tan δ)$_{max}$) and shifted towards higher temperatures. Using the relationship:

$$f = f_0 e^{-W_d/KT}, \tag{1}$$

the effective activation energy W_d for the dipoles is calculated for these glasses and is found to decrease with increase in Bi$_2$O$_3$ concentration up to 12% of Bi$_2$O$_3$ (glass C) and found to increase with further increase in the concentration of Bi$_2$O$_3$ (Inset of Fig. 6).

The ac conductivity σ is calculated at different temperatures using the equation

$$\sigma = \omega \varepsilon_0 \varepsilon' \tan \delta, \tag{2}$$

(where ε_0 is the vacuum dielectric constant) for different frequencies and the plot of log σ against $1/T$ is shown in Fig. 7a for glass D. Plots also drawn for other glasses have exhibited similar behavior. From these plots the activation energy for conduction in the high temperature region over which a near linear dependence of log σ with $1/T$ could be observed, is calculated and presented in Table I.

The variation of conductivity and activation energy with the concentration of Bi$_2$O$_3$ is shown in Fig. 7b. The conductivity σ is found to increase with the concentration of Bi$_2$O$_3$ and reaches a maximum at 12%, where as activation energy decreases and reaches a minimum value for the same concentration.

The dielectric break down strength at room temperatures for glass A is determined to be 18.81 kV/cm; the value of breakdown strength is found to be minimum for glass C (Table I).

Fig. 8 shows infrared transmission spectra of ZnF$_2$-Bi$_2$O$_3$-TeO$_2$ glasses along with that of crystalline TeO$_2$ and Bi$_2$O$_3$. IR spectrum of crystalline TeO$_2$ exhibited two absorption bands at 772 cm^{-1} [ν_1(A$_1$)] and
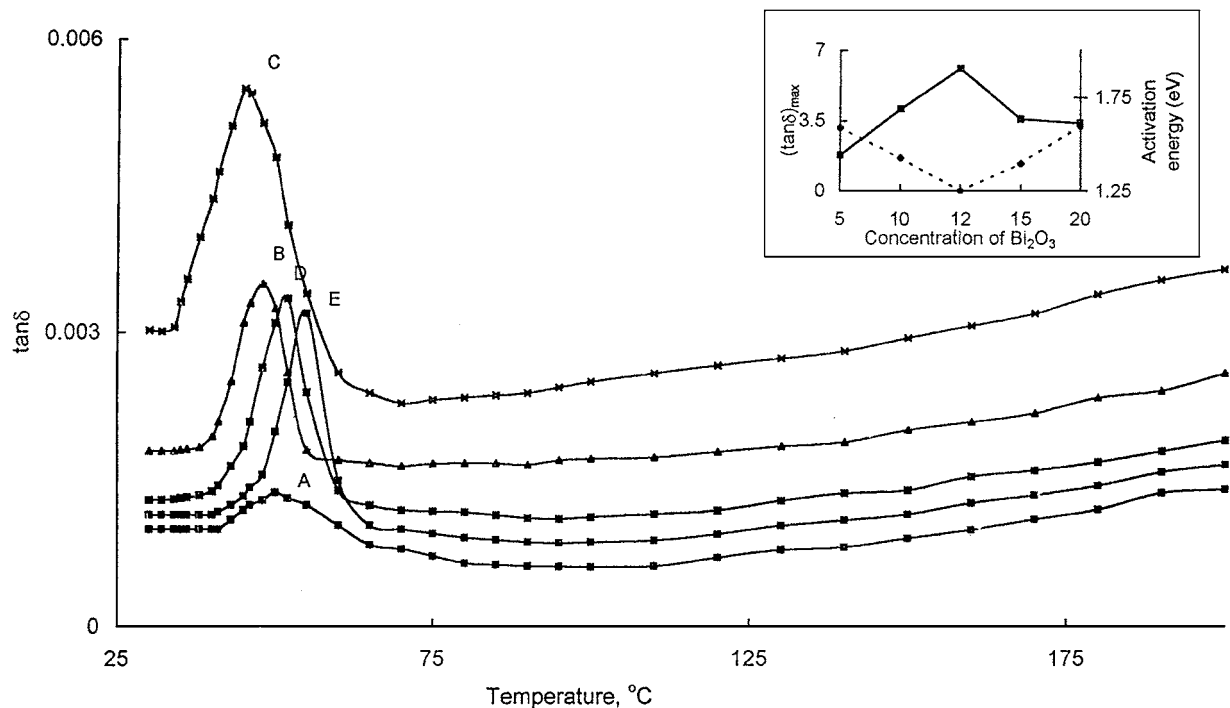
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Figure 6 Comparison plot of tan δ with temperature for ZnF_2-Bi_2O_3-TeO_2 glasses measured at 100 kHz, inset shows variation of $(\tan \delta)_{max}$ (solid line) and activation energy for dipoles (dotted line) with concentration of Bi_2O_3.

650 cm^{-1} $[\nu_2(A_2)]$ which can be attributed to $\nu^s_{TeO_2eq}$ and $\nu^s_{TeO_2ax}$ with C_{2v} symmetry, respectively [16].

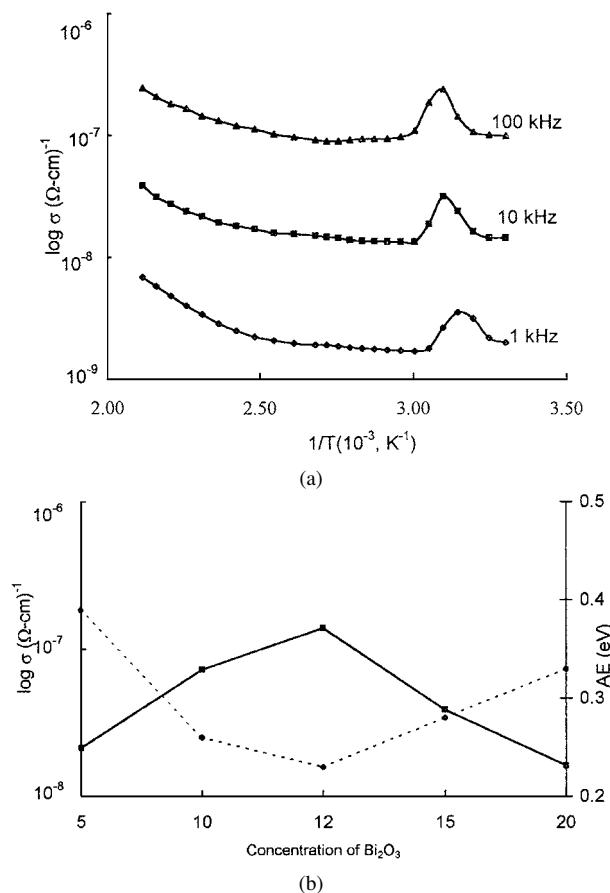In the infrared spectrum of glass A, band at 650 cm^{-1} (axial band) is found to be shifted to 642.6 cm^{-1}

Figure 7 (a) Variation of σ with $1/T$ at different frequencies for glass D; (b) Variation of conductivity at 200°C (10 K) (solid line) and the associated activation energy (dotted line) with Bi_2O_3 content.

where as the band at 772 cm^{-1} (equatorial band) has completely disappeared; with increase in concentration of Bi_2O_3 (up to 12%), $(\nu_2(A_2))$-axial band is shifted towards higher frequencies with decreasing intensity. When the concentration of $Bi_2O_3 > 12\%$, this band is shifted towards lower frequencies with slight increase in intensity (Table II). The spectra of these glasses have also exhibited intense bands between 1089–1094 cm^{-1} with increasing intensity with Bi_2O_3 concentration; these bands are presumably due to the presence of BiO_nF_m polyhedra in ZnF_2-Bi_2O_3-TeO_2 glass network [17]. In addition there is a band between 400–500 cm^{-1} in these glasses. The crystalline Bi_2O_3 exhibits three active fundamental absorption bands (out of four expected bands) at 839.3 (ν_1), 550 (ν_3), 475 (ν_2) cm^{-1}; these bands are identified as, ν_1 (a totally symmetric stretching vibration), ν_3 (a doubly degenerate stretching vibration), ν_2 (a totally symmetric bending vibration) of Bi_2O_3 pyramidal units of point group C_{3v} [18, 19]. When Bi_2O_3 is in the glass matrix, ν_1 and ν_3 bands disappeared except a band due to ν_2 vibrations; in glass A this band is observed at 423.5 cm^{-1}. Increase in the concentration of Bi_2O_3 from 5% (glass A) to 12% (glass C) this band is shifted to 497 cm^{-1}. When Bi_2O_3 concentration increases this band is found to shift towards lower frequencies (Table II).

4. Discussion

TeO_2 belongs to intermediate class of glass forming oxides; it is an incipient glass network former and as such does not readily form glass because the octahedral Te-O polyhedron is highly rigid (when compared with other glass forming oxides like GeO_2 etc.) to get required distortion of Te-O bonds, necessary for forming a stable network. Earlier neutron scattering experiments [20] and Raman spectral studies [21, 22] on TeO_2 glasses

TABLE I Data on a.c. conductivity σ and breakdown strengths for ZnF_2-Bi_2O_3-TeO_2 glasses

| Glass | $N(E_F)$ in (10^{20}, eV^{-1}/cm^3) according to | | | S_{exp} | Activation energy (eV) | | Breakdown strength (kV/cm) |
	Austin and Mott	Butcher and Hyder	Polak		$\sigma_{a.c}$	$\Delta\varepsilon'$	
A	0.20	0.08	0.21	0.91	0.39	0.41	18.81
B	0.36	0.15	0.37	0.88	0.26	0.28	16.93
C	0.51	0.21	0.52	0.86	0.23	0.22	12.58
D	0.26	0.11	0.27	0.87	0.28	0.30	17.10
E	0.22	0.09	0.23	0.90	0.33	0.35	17.32

containing different modifiers have revealed that the basic building block of TeO_2 glass structure is a trigonal bipyramid commonly called TeO_4E, where one of the three equatorial directions is occupied by the $5s^2$ electronic pair (E) of the tellurium atom with two equatorial bonds of lengths 1.91 Å and two axial bonds of lengths 2.08 Å [23–25]. The environment of these Te atoms is completed by two other longer interactions of lengths 2.9 Å and the three dimensional close packing is constituted from vertices sharing TeO_4 groups (Te_{eq}-O_{ax}-Te) reinforced by weaker Te-O interactions of lengths 2.9 Å [16, 26]. In general ZnF_2 acts as modifier, fluorine ions break the Te-O bonds while Zn^{2+} ions may occupy interstitial positions or form Zn-O-Te linkages because of the close ionic radii of Te^{4+} (0.7 Å) and Zn^{2+} (0.74 Å) ions. Bi_2O_3 on the other hand acts both as modifier (with BiO_6 octahedral units) and as network former (with BiO_3 pyramidal units) because of the high polarisability of bismuth ion, and due to the presence of a $6s^2$ stereo chemically active electronic lone pair [27].

As a modifier, Bi_2O_3 enters the glass lattice network by breaking up Zn-O-Te bonds and TeO_4 bonds and may introduce: (i) the stable Te-Ō and (ii) unstable Te-Ō bonds which will later be modified to Te-Ō (or simply TeO_{3+1}) owing to the contraction of one Te-Ō and the elongation of another Te-Ō bond. With increasing Bi_2O_3 content (up to 12%), cleavage of continuous network leads to an increase in the fraction of TeO_{3+1} polyhedra. Further the elongation of Te-O bond

TABLE II Positions of the absorption bands in the infrared spectra of ZnF_2-Bi_2O_3-TeO_2 glasses

Glass	Band 1 cm^{-1}	Band 2 cm^{-1}	Band 3 cm^{-1}
A	423.5	642.6	1093.5
B	467.6	669.9	1089.2
C	497.0	672.1	1093.4
D	462.4	637.4	1092.8
E	422.4	627.4	1091.7
Crystalline TeO_2	649.8 (v_{ax}^s), 772 (v_{eq}^2)		
Crystalline Bi_2O_3	475 (v_2), 550 (v_3), 859.3 (v_1)		

of TeO_{3+1} and its cleavage finally lead to the formation of trigonal prismatic TeO_3 units. Thus in addition to Te-O-Te, Zn-O-Te linkages, the structure of the present glass network consists of TeO_4, TeO_{3+1} and TeO_3, free Zn^{2+} ions, free F^- ions and non bridging oxygens. Such bonding defects may increase with increase in the concentration of Bi_2O_3.

Among various polarizations, that contribute to the dielectric constant, the contribution from the space charge polarization depends on the purity and perfection of the glasses. The gradual increase of ε', $\tan\delta$ (beyond the relaxation region) and also conductivity, with increase in the concentration of Bi_2O_3 up to 12%, may be ascribed to increase in bonding defects which contribute to the space charge polarization. This indicates Bi_2O_3 acts as modifier (in addition to ZnF_2) with BiO_6 structural units in ZnF_2-Bi_2O_3-TeO_2 glass
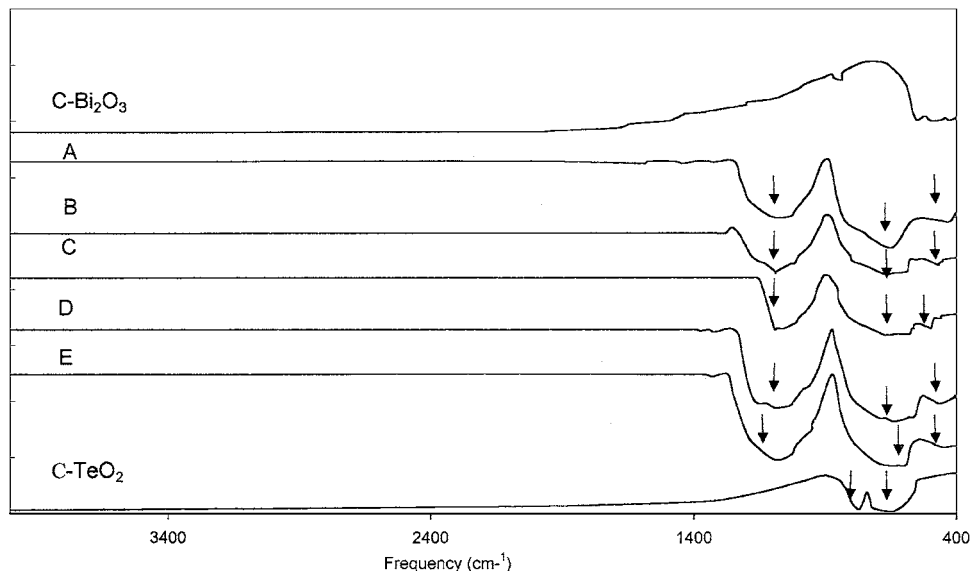

Figure 8 Infrared spectra of ZnF_2-Bi_2O_3-TeO_2 glasses along with crystalline TeO_2 and Bi_2O_3.

network up to this concentration. This is also supported by the fact that the symmetrical vibrational frequencies of ν_{ax}^s-bonds of TeO$_4$ groups are shifted towards higher frequencies with decreasing intensity for such concentrations. The decrease in glass transition temperature and other related parameters [Fig. 2] with increase in Bi$_2$O$_3$ concentration, also support the increasing modifying action of Bi$_2$O$_3$ in this concentration region.

It is observed that, when the concentration of Bi$_2$O$_3$ is increased beyond 12%, the values of ε', $\tan\delta$ and σ decrease with increase in the concentration of Bi$_2$O$_3$; this is due to decrease in the distortion of glass network, which in turn reduces the space charge polarization. At such higher concentrations, Bi$_2$O$_3$ may participate in the glass network with BiO$_3$ pyramidal units. In addition, there is also a possibility for Bi$_2$O$_3$ molecules to form BiO$_n$F$_m$ polyhedra complexes making the glass structure more stronger. The concentration of such complexes may increase with increase in the concentration of Bi$_2$O$_3$. The increase in the intensity of the vibrational band at about 1090 cm^{-1} due to BiO$_n$F$_m$ polyhedra, indicates an increase in the concentration of such Bi-O-F linkages, which in turn reduce the concentration of free F$^-$ ions and oxygen ions. Such reduction in the free charge carriers, decreases the space charge polarization, leading to a decrease in the dielectric parameters viz., ε', $\tan\delta$ and σ. The increase in the glass transition temperature [Fig. 2] beyond 12% of Bi$_2$O$_3$ also suggests the increase in the rigidity of the glass network [28, 29].

Among the three constituents viz., ZnF$_2$, Bi$_2$O$_3$ and TeO$_2$ of these glasses, the bonds of tellurium with oxygen are known to be polar in nature [30] and hence it is reasonable to attribute the observed dipolar effects in these glasses to the TeO$_2$ molecules [2, 31]. Increase in $(\tan\delta)_{max}$ and broadening of relaxation curves [Fig. 6] with increase in Bi$_2$O$_3$ concentration (up to 12%) indicate the spreading of relaxation times in these glasses [32]; this may be understood due to the experience of an approximately random potential energy by the dipoles on diffusing through the distorted structure of the glass [33]. The decrease in the activation energy for dipoles [Fig. 6 inset] with increase in the concentration of Bi$_2$O$_3$ up to 12% indicates an increase in the distortion of the glass network, thus making dipoles more and more free to orient along the field direction. This also indirectly supports the modifying action of Bi$_2$O$_3$ molecules up to this concentration. The increase in the activation energy, beyond 12% concentration of Bi$_2$O$_3$, indicates a decrease in the distortion of glass network due to the participation of these molecules in the network forming positions.

It is interesting to find that the nature of variation of ε' and $\tan\delta$ with temperature is similar. The variation of ε' with temperature can be connected to frequency through modified Debye equation as reported earlier [1, 34]. A plot of log ($\Delta\varepsilon'$) against $1/T$ (where $\Delta\varepsilon'$ is the difference between dielectric constant at any temperature T and that at room temperature) at different frequencies for (glass B) is shown in Fig. 9; the graphs are straight lines having about the same slope for all the frequencies in the high temperature region.
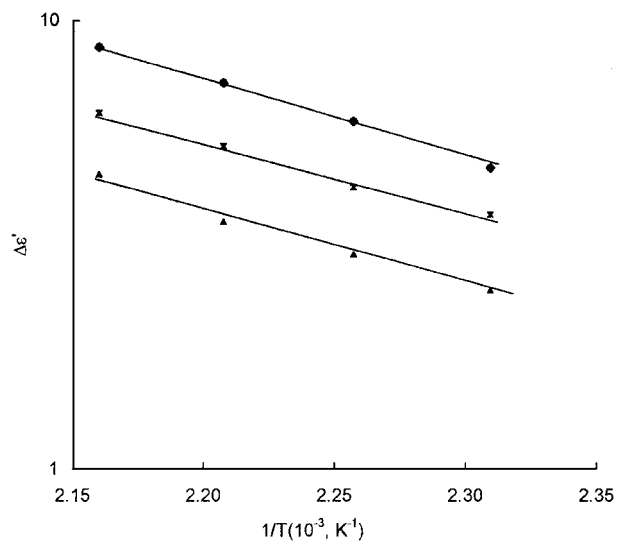

Figure 9 Variation for $\Delta\varepsilon'$ with $1/T$ at different frequencies for glass B.

The computed activation energy is 0.28 eV for glass B. This value is practically the same as the activation energy for ac conduction in the same temperature region in these glasses. This seems to suggest that the charge carriers responsible for change in ε' and σ with temperature in this temperature range are the same. A similar analysis was also carried out on the other glasses and found to yield the similar result (Table I).

It can be stated here that the increase in conductivity and decrease in activation energy with increase in concentration of Bi$_2$O$_3$ up to 12% is obviously due to increase in the free charge carriers which may find easy paths for migration in the distorted structure [3]. When a plot is made between log σ (ω) vs activation energy for conduction, a linear relationship is observed (up to glass C) [Fig. 10b]; this suggests the increase in conductivity is mainly due to the increase in the mobility of the charge carriers [3].

The variation of ac conductivity with the concentration of Bi$_2$O$_3$ in the low temperature region up to 50°C can be explained on the basis of QMT model. The ac conductivity of the amorphous material, where the charge carriers experience an approximately random potential energy in diffusing, is found to obey the equation [35]:

$$\sigma(\omega) = A\omega^s \qquad (3)$$

with the exponent $s < 1$ (upto the frequency 1 MHz), is considered to signify the coupling of an ion's movement with its environment [35, 36].

Though various models have been developed to interpret the ac conduction mechanism in the glasses, we have first attempted to explain ac conduction in the present ZnF$_2$-Bi$_2$O$_3$-TeO$_2$ glasses on the basis of quantum mechanical tunneling (QMT) model.

According to QMT model, only those pairs of carriers separated by hopping distance R_ω given by:

$$R_\omega = (1/2\alpha) \ln\left(\frac{\nu_{ph}}{\omega}\right) \qquad (4)$$

contribute significantly to conduction. With this, the equation for ac conductivity due to quantum mechanical tunneling is given by [35]:
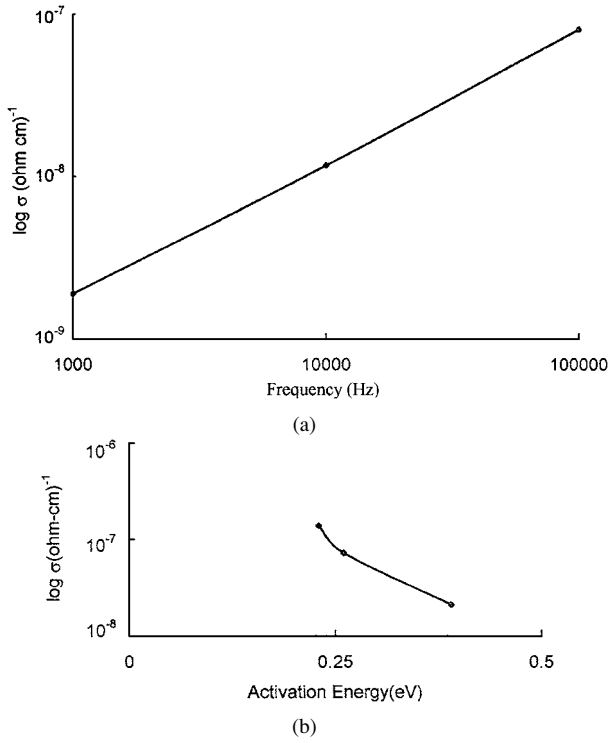
(a)

(b)

Figure 10 (a) Variation of conductivity ($\log \sigma$) with frequency for glass E; (b) Variation of $\log \sigma$ at 200°C (10 K) (up to glass C) with activation energy for conduction.

$$\sigma(\omega) = \eta e^2 KT [NE_F]^2 \alpha^{-5} \omega \left[\ln \frac{\nu_{ph}}{\omega} \right]^4 \qquad (5)$$

where $N[E_F]$ is the density of energy states near the Fermi level, α is the electronic wave function decay constant and its average value is determined from $\sigma = e^{-2\alpha Ri}$, ν_{ph} is phonon frequency ($\sim 5 \times 10^{12}$ Hz) and η is a constant and its value is given by: $\eta = \pi/3$ [Ref. 35], $\eta = 3.66\pi^2$ [Ref. 37], $= \pi^4/96$ [Ref. 38].

The frequency exponent s is defined as:

$$s = \partial(\ln \sigma)/\partial(\ln \omega) \qquad (6)$$

Substitution of Equation 5 in Equation 6 results in

$$s = 1 - \frac{4}{\ln(1/\omega\tau_0)} \qquad (7)$$

Thus the quantum mechanical tunneling of a carrier through the potential barrier between the sites separated by a distance R_ω demands that 's' should be independent of temperature.

The plot of $\log \sigma(\omega)$ versus $\log \omega$ for (glass E) at a temperature of 318 K is shown in Fig. 10a. The graph obtained is a straight line. Plots drawn for the other glasses have also yielded straight lines.

Among various mechanisms for conduction in the amorphous materials, the conduction in the localized states near the Fermi level occurs when ac conductivity is nearly temperature independent and varies linearly with frequency. The conduction in present ZnF_2-Bi_2O_3-TeO_2 glasses in the low temperature region (up to 318 K) can be safely attributed to take place by this mechanism. The value of $N[E_F]$, i.e. the density of energy states near the Fermi level is calculated using Equation 5, with value of numerical constant η
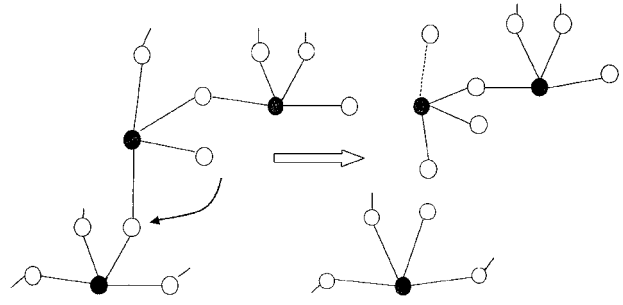

Figure 11 A mechanism for structural change in TeO$_2$ glassnetwork from TeO$_4$(tbp) to TeO$_{3+1}$ polyhedra induced by modifier, ● - Te, ○ - Oxygen and the arrow indicates modifier entry.

suggested by different investigators and presented in Table I. The value of $N[E_F]$ is found to be maximum for glass C. Further the range of $N[E_F]$ values obtained $\sim 10^{20}$ eV^{-1}/cm^3. Such values of $N[E_F]$ suggest the localized states near the Fermi level [33]. The increase in the conductivity from glass A to C can be understood due to the increase in the density of these energy states. Further, the decrease in conductivity from glass C to E is due to the decrease in the density of energy states.

When the dielectric is placed in the electric field, the heat of dielectric loss is liberated. If the applied field is an alternating field, the specific dielectric loss i.e., the loss per unit volume of the dielectric is given by [39]:

$$\rho_1 = E^2 \omega \varepsilon \varepsilon_0 \tan \delta \text{ W/m}^3. \qquad (8)$$

This equation indicates that the higher the values of $\varepsilon' \tan \delta$ of the glass at a given frequency, the higher are the losses. In a dielectric across which the voltage is applied, heat is liberated, the temperature of the dielectric then rises and the loss increases still more. The dielectric breakdown strength is in fact inversely proportional to the specific dielectric loss represented by Equation 8.

The observations on breakdown strengths of ZnF_2-Bi_2O_3-TeO_2 glasses, as mentioned earlier, indicate, the increase of $\varepsilon' \tan \delta$ with temperature is highest for glass C. Though the breakdown strengths are actually determined at room temperature, the heat liberated during the breakdown, raises the temperature of the glass and hence raises the $\varepsilon' \tan \delta$ value. Since the rate of increase of $\varepsilon' \tan \delta$ with temperature is the highest for glass C, the breakdown strength is lowest when compared with the other glasses. Thus the experiments on the dielectric breakdown strength of ZnF_2-Bi_2O_3-TeO_2 glasses reveal that there is an increase in the disorderliness in the glasses with increase in the concentration of Bi^{3+} ions up to 12%. It is further supporting the modifier action of Bi_2O_3 when it is present at about this concentration in the present glass network.

Finally the analysis of the results of various measurements viz., dielectric parameters (ε', $\tan \delta$, σ and dielectric breakdown strength), IR spectra and DTA on ZnF_2-Bi_2O_3-TeO_2 glasses indicate that these glasses are more stable, if the concentration of Bi_2O_3 is over and above 12% in the glass network.

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