EFFECT OF TiO₂ ADDITION ON ELASTIC MODULI, OPTICAL BANDGAP, AND ELECTRICAL CONDUCTIVITY OF xTiO₂-(0.30-x)Bi₂O₃-0.10ZnO-0.60TeO₂ GLASSY SYSTEMS WITH IMPROVED THERMAL STABILITY

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SUMMARY

Glassy systems with the chemical composition $xTiO_2$ -(0.30-x)Bi₂O₃-0.10ZnO-0.60TeO₂ (x = 0.05,0.10,0.15,0.20) have been synthesized using the melt quench approach. Numerous physical, electrical, optical, and other features of elastic moduli have been evaluated as titanium oxide concentration rises. The amorphous properties of the materials under inspection are displayed in the XRD pattern. As the concentration of arsenic rises, the glasses' density falls from 4.18 to 3.96 g/cm³, while their molar volume rises from 48.21 to 53.06 cm³mol⁻¹. The elastic properties of the synthesized glasses, such as the shear (S) and longitudinal (L) stresses, bulk modulus (K), Young's modulus (Y), and Poisson's ratio (Pr), have all been measured using the measured values of the ultrasonic velocities. The increase in elastic moduli values showed that the materials' elastic qualities have been improved. The results are explained in terms of a significant structural alteration caused by molecular rearrangement, which controls the physical properties of the glass. The addition of titanium oxide is shown to cause a decrease in Urbach energies from 0.96 to 0.67 eV, which results in an increase in the optical band gap energies from 2.96 to 3.33 eV. DSC thermogram measurements reveal mechanically enhanced and thermally stable materials with potential for use in semiconducting devices.

KEYWORDS

Young's modulus, Optical band gap energy, DC conductivity, DSC thermogram

1. INTRODUCTION

Tellurite-based glasses often surpass phosphates, germinates, and silicates in physical and optical properties (Mandal et al., 2023). Tellurite glass features a high refractive index, making it attractive for various optoelectronic applications (El-Mallawany et al., 2021). Researchers are increasingly exploring TeO2-based glasses for applications in high-performance lasers, broadband amplifiers, optical fibers, light-emitting materials, telecommunications, and other advanced technologies. (Biswas and Jana, 2023). Adding modifying oxides, which act as network modifiers, is common practice to stabilize tellurite glass due to TeO2's poor glass-forming ability (Mondal et al., 2020). ZnO reduces the crystallization rate and lowers the melting point, enhancing glassforming potential (Mondal et al., 2020). It is anticipated that Oxide modifiers can break certain TeO4 units in tellurite glasses. Te ion coordination numbers concerning oxygen ions shift, causing tellurite's structural units to transform from a trigonal bi-pyramid TeO₄ to a distorted polyhedron TeO_{3+1} and finally a trigonal pyramid (t_p) TeO₃ (Lucacel et al., 2010). Tellurium ion coordination modification produces both bridging and non-bridging oxygen, which interacts with neighboring tellurium atoms to create modifier atoms (Sidek et al., 2009). Because of its functions as a modulator and network former in the glass network, bismuth oxide (Bi₂O₃) stands out among heavy metal oxides when added to tellurite glasses (Shaaban and Yousef, 2020). Bi₂O₃ addition increases the glasses' stability and chemical resistance. By raising density and refractive index, Bi₂O₃ serves as both a glass forming and a glass modifier (Rao et al., 1985). Glasses with heavy metal oxide modifiers like Bi₂O₃ enhance transmission windows and nonlinear optical traits in tellurite glasses, making them promising for photonics, signal processing, and

optoelectronics (Berwal et al., 2017). Researchers have studied Bi₂O₂ incorporated tertiary tellurite-based glass in several investigations. In the interim, additives like Gd₂O₃, Cr₂O₃, CaF₂, Fe₂O₃, TiO₂, etc. are typically added to the base system as property modifiers to generate more sophisticated glassy systems (Hathot et al., 2021, Zhang et al., 2019). TiO₂'s addition attracts attention for enhancing glassy systems' electrical, mechanical, spectroscopic properties, and thermal stability, among others (Osipov et al., 2020). Additionally, it has been discovered that TeO₂-based glassy systems have been promising and had applications in laser-operated devices (Narasimha Rao et al., 2012). However, due to the stiffness of the octahedral Te-O polyhedron, TeO₂ is an emerging glass former that is difficult to form glass alone under typical synthesising circumstances (Elkhoshkhany and Syala, 2017).

In previous studies, Murugan et, al have studied temperature assisted electrical properties of TeO_2 -Bi₂O₃-ZnO glasses (Murugan et al., 2004), Kabalci et.al have studied the structure, and hardness competence of TeO_2 -Bi₂O₃-ZnO glasses (Kabalci et al., 2017), Fong et.al have studied the thermal, and optical properties of Bi₂O₃-TiO₂-Na₂O-ZnO-TeO₂ glasses (Fong et al., 2021) for various optoelectronic applications. Recent research explores nanocomposites for potential in photonics and dielectric applications (Al-Muntaser et al., 2022).

The primary objective of the current work is to gain a deep realization of the role of TiO_2 on the glass network structure, and electrical, mechanical, and optical properties of $\text{TiO}_2\text{-Bi}_2\text{O}_3\text{-ZnO-TeO}_2$ glassy systems in addition to investigating its capability as an electro-optical material in semiconducting photonic device applications, thereby contributing to the advancement of glass nanocomposite technology for various applications.

2. MATERIALS AND METHODS

2.1 SAMPLE PREPARATION

The $xTiO_2$ -(0.30-x)Bi₂O₃-0.10ZnO-0.60TeO₂ (x = 0.05, 0.10, 0.15, 0.20) quaternary glass nanocomposites were prepared by finely crushing precise quantities of highpurity raw chemicals, including TeO2, Bi2O3, TiO2, and ZnO (99.9% as pure), in an agate mortar to achieve a homogeneous powder. The mixtures were heated in alumina crucibles in an electric furnace under atmospheric air conditions until reaching melting points, ranging from 1100-1200 °C. Each stage of the melting process requires careful observation. To enhance melt fluidity, it was kept at the melting temperature in an electric furnace for 30 extra minutes. The melts were swiftly quenched at room temperature using a polished aluminum melt-quencher, yielding glassy flakes 0.3 to 0.5 mm thick. The prepared samples were annealed at 350°C to alleviate internal stress from the quenching process.

2.2 PHYSICAL MEASUREMENT TECHNIQUE

Molecular weight, constituent proportions, and glass structure collectively impact oxide glass density (ρ). The Archimedes equation (Eq. (1)) determined glassy systems' densities using acetone as the immersion liquid (Singh et al., 2021b).

$$\rho = \rho_{acetone} \left(\frac{W_{air}}{W_{air} - W_{acetone}} \right) \tag{1}$$

In Eq. 1, W_{air} and $W_{acetone}$ are the measured weights of the glass sample in air and acetone, respectively, while pacetone is acetone's density. The density (ρ) of each glass sample was determined from three pieces, and an average was taken to reduce inaccuracies. Weights were measured using a digital balance with a precision of 10^{-4} g.

The molar volume (V_M) of the glass system, a crucial physical parameter, can be calculated using Eq. (2), which incorporates the molecular weight (M) and the estimated density (ρ) of the glass system (Singh et al., 2021b).

$$V_{M} = \sum \frac{x_{i}M_{i}}{\rho} \tag{2}$$

In Eq. (2), x_i and M_i represent the molar fraction and molecular weight of the i^{th} glass composition, respectively.

2.3 CHARACTERIZATION TECHNIQUE

A study employing X-ray diffraction (XRD) was conducted on each glass sample to verify its amorphous nature. Rigaku TTRAX-III XRD diffractometer was used, with CuKa radiation ($\lambda = 1.541$ Å), scanning at 4°/min with a step size of 0.02 over 15 to 80 degrees.

2.4 MEASUREMENT OF MECHANICAL PARAMETERS

The study utilized an ultrasonic flow detector (USN 60) with the pulse-echo-overlap technique at room temperature. Longitudinal and shear transducers with a frequency of 5MHz were employed. Ultrasonic velocity (v) was determined by selecting the first two echo signals (A1, A2) and their corresponding times (t1, t2) in the sample (Saddeek et al., 2010),

$$\upsilon = \frac{2X}{t_2 - t_1} \tag{3}$$

Here, with pulse time (t) in seconds and sample thickness (X), shear (S) and longitudinal (L) strains were calculated using measured values of \mathbf{v}_{L} , \mathbf{v}_{T} and ρ following specific relations. $L = \rho v_{L}^{2}$, and $S = \rho v_{T}^{2}$ (Saddeek et al., 2019). The Poisson ratio (Pr), Young (Y), and Bulk (K) moduli

were calculated by calculating the S and L values in the manner described below (Saddeek et al., 2019) [35]:

$$K = L - 1.33S \tag{4}$$

$$P_r = (L - 2S)(2L - 2S)^{-1}$$
(5)

$$Y = 2S\left(1 + P_r\right) \tag{6}$$

2.5 DIRECT CURRENT MEASUREMENTS

High-temperature conductive silver paste was applied to bulk materials in order to prepare them as electrodes for electrical research. A two-point probe method was used to test the DC electrical conductivity. Using a digital multimeter, sample resistances quenched at different temperatures were determined. A calibrated thermocouple that was positioned close to the sample in the furnace was used to track the temperature. With a \pm 5% error tolerance, the temperature controller unit and thermocouple were utilized to accurately calculate the glass's operating temperature. Between 423 K and 623 K, the temperature dependency of DC electrical conductivity was carefully assessed.

2.6 OPTICAL MEASUREMENTS

Optical absorption spectra (190–700 nm) were acquired at room temperature using a Shimadzu NIR 3600 UV– Vis spectrophotometer in reflectance mode. Colloidal suspensions for absorption were prepared by homogenizing fine powder glass samples in ethyl alcohol with an ultrasonic sonicator (Takashi SK-500F). If we assume the indirect transition, we may express the absorption coefficient (α) as follows (Biswas et al., 2023):

$$\left(\alpha h \upsilon\right)^{1/2} = B(h \upsilon - E_{opt}) \tag{7}$$

In this case, the optical band gap energy is represented by E_{opt} , the photon energy is represented by hu, and the constant parameter is B. Tauc's plot is the plot of $(\alpha h u)^{1/2}$ against hu (Biswas et al., 2023).

Here,
$$\alpha(\upsilon) = 2.303 \frac{Absorbance}{samplethickness}$$
 (8)

3. RESULT AND DISCUSSION

3.1 X-RAY DIFFRACTION

As depicted in Figure 1, the XRD patterns of the $xTiO_2$ -(0.30-x)Bi₂O₃-0.10ZnO-0.60TeO₂ samples illustrates no significant peaks aside from the broad peak due to glass structure. The materials lack crystallinity, displaying

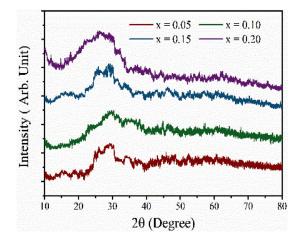


Figure 1. XRD patterns glassy systems

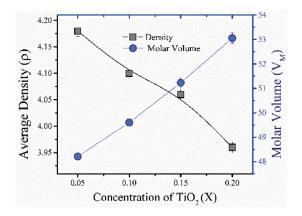


Figure 2. Variation of density and molar volume with TiO_2 content (x)

a broad hump (20–40 degrees) without sharp peaks, suggesting a non-crystalline, amorphous, or short-range ordered structure (Mondal et al., 2023).

3.2 STUDY OF DENSITY AND MOLAR VOLUME

Density is a key factor in understanding structural changes and compactness in the glass network, influencing thermal, elastic, and optical properties. Computed density (ρ) values, obtained using Eq. 1, are plotted against TiO₂ concentration (x) in Figure 2. Molar volume, vital for analyzing structural characteristics, is correlated with density.

Eq. 2 can be used to find the glassy system's molar volume. As shown in some earlier research, it is evident from Figure 2 that there is an inverse relationship between density and molar volume. All the obtained values of densities and molar volumes

X	Density (ρ) g/cm ³	Molar volume (V _M) cm ³	Bandgap energy (E _{opt}) eV	Urbach energy (ΔE) eV
0.05	4.18	48.21	2.96	0.96
0.10	4.10	49.60	3.05	0.87
0.15	4.06	51.23	3.27	0.72
0.20	3.96	53.06	3.33	0.67

Table 1. Obtained physical, and optical parameters of studied glass samples

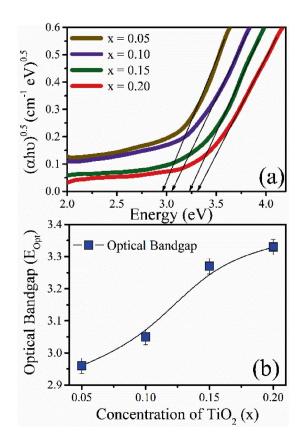


Figure 3. (a) Tauc's plot of studied samples, (b) variation of E_g Titanium oxide content (x)

are tabulated in Table 1. The decrease in density (ρ) is attributed to the replacement of higher-density Bismuth oxide with lower-density Titanium oxide atoms (Elkhoshkhany et al., 2016). The increase in molar volume (VM) results from lattice rearrangement due to TiO₂ replacing Bi₂O₃, expanding the structure and increasing the ring size (Elkhoshkhany et al., 2016).

3.3 STUDY OF OPTICAL BAND GAP ENERGY AND URBACH ENERGY

Disordered materials show an absorption edge attributed to indirect transitions across an optical gap, as explained by the electronic structure theory of amorphous materials.

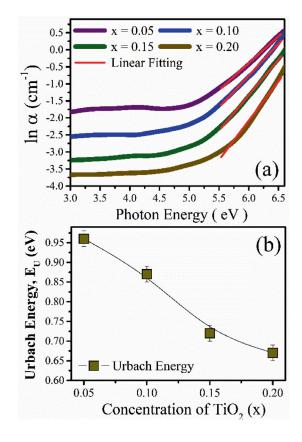


Figure 4. (a) variation of ln (α) against hv (b) variation of E_U with Titanium oxide content(x)

By taking a graph of the variation of $(\alpha h \upsilon)^{1/2}$ vs h υ and projecting the linear region to the x-axis when $\alpha = 0$ of the curves, one can use a Tauc approach to get optical energy band gap values (Figure 3(a)) (Singh et al., 2021a).

Table 1 and Figure 3(b) summarize E_g values for glasses with varying titanium oxide percentages. As titanium oxide content increases, replacing bismuth oxide, the band gap energy grows from 2.96 to 3.33 eV. This rise may be attributed to the higher band gap energy of titanium oxide compared to bismuth oxide. Additionally, a decrease in Urbach energy levels could contribute to the increasing E_{opt} value.

To assess disorder in materials, Urbach energy (E_U) is crucial. The band tail width (E_U) is associated with electron transitions between localized states, exhibiting an exponential pattern due to random potential variations in the material's energy released into the bandgap. Regardless of substance composition, the experimental tail stems from localized states within the restricted band-gap region.

The Urbach energy (E_U) can be obtained by plotting $ln(\alpha)$ against photon energy (Figure 4(a)) and using the empirical relation (Urbach, 1953):

$$\alpha(\upsilon) = \alpha_0 exp\left(\frac{h\upsilon}{\Delta E}\right) \tag{9}$$

The resulting values of $E_{\rm U}$ are shown in Figure 4(b). It's interesting to note that as titanium oxide is incorporated into the host matrix in greater numbers, Urbach energy drops, which raises the $E_{\rm opt}$ of the materials under study (Table 1). Previous studies have indicated an inverse relationship between the $E_{\rm g}$ and $E_{\rm U}$ (El Ghandoor et al., 2012).

3.4 STUDY OF ULTRASONIC WAVE VELOCITIES AND ELASTIC MODULI

Table 2 lists the longitudinal velocity (v_L) and shear velocity (v_T) data that were acquired and recorded at room temperature. Figure 5 shows how the Titanium content (x) varies with longitudinal and shear velocities.

With increased Titanium oxide in the glassy matrix, both \mathbf{v}_{L} , \mathbf{v}_{T} rise from 3132 m/s to 3274 m/s and from 1796 m/s to 1878 m/s, respectively. This increase in ultrasonic velocities is attributed to structural changes, molar volume increase, and impedance decrease in the studied glasses. Computed longitudinal modulus (L) and shear modulus (S) rise from 41.00 to 42.66 Gpa and 13.48 to 14.03 Gpa, respectively, as shown in Table 2. Bulk modulus (K), Young's modulus (Y), and Poisson ratio (Pr) values also increase with the addition of Titanium oxide. The elasticity bulk modulus is a crucial mechanical measure for assessing a substance's compression under external pressure. The elastic moduli are extremely significant parameter for a

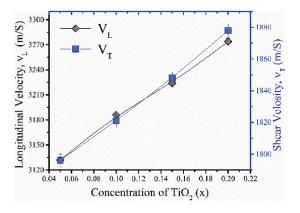


Figure 5. Variation of longitudinal velocity (\mathbf{v}_L) , and shear velocity (\mathbf{v}_T) of studied glasses with Titanium oxide content (x)

Table 2. The mechanical parameters of the studied glasses

x	v _L m/s	v _T m/s	S Gpa	L Gpa	K Gpa	P _r Gpa	Y Gpa
2	3132	1796	13.48	41.00	23.08	0.257	33.75
4	3186	1821	13.59	41.61	23.54	0.256	34.15
6	3224	1848	13.86	42.20	23.77	0.254	34.78
8	3274	1878	14.03	42.66	24.01	0.253	35.18

material to inspect to examine the functionalization of that sample (Yadav et al., 2019). The observed increasing trend of Pr (from 0.252-0.254) Gpa signifies good mechanical strength of the studied glasses. It has been demonstrated in the literature that even trace amounts of Titanium oxide can change average connectivity, which in turn can modify crosslink density and, in turn, elastic moduli ,as found in previous study [38].

3.5 DC CONDUCTIVITY

The figure reveals two distinct temperature-dependent conductivities (σ_{dc}) in glassy systems, emphasizing varied conductive behaviors. The non-linear σ_{dc} behavior, increasing with temperature across all systems, strongly supports their inherent semiconducting nature. The amorphous glassy structure introduces extended or localized states within the mobility gap, influencing intricate electronic properties. These states play a crucial role in dictating electrical conductivity, particularly at higher temperatures, where band conduction relies on charge carriers moving across these states. The semiconducting behavior is further confirmed by the Arrhenius equation characterizing the σ_{dc} (Mandal et al., 2023).

$$\sigma_{dc} = \sigma_{High} \exp\left(-\frac{E_{High}}{K_B T}\right) + \sigma_{Low} \exp\left(-\frac{E_{Low}}{K_B T}\right)$$
(10)

Conversely, at lower temperatures, the conduction process is dominated by the presence of small polarons or electrons engaging in hopping behaviour (Biswas et al., 2019a). Charge carriers move through different states in the material, including localized, extended, or defect states. Tunnelling between nearby sites also aids conduction at lower temperatures. The intricate interplay between charge carriers and varied conduction mechanisms at different temperature ranges underscores the complexity of semiconducting behavior in glassy systems. The diverse mechanisms in different temperature regimes offer a comprehensive understanding of conductivity phenomena in these materials.

Figure 6 shows σ_{dc} spectra plotted against the reciprocal of temperature, confirming two distinct forms of temperature-dependent σ_{dc} . The non-linear behavior in dc conductivity (σ_{dc}) and the simultaneous increase in σ_{dc} with rising temperature across all glassy systems affirm their inherent semiconducting characteristics. This suggests semiconductor-like properties in electrical conductivity, influenced by temperature changes akin to semiconductors. Eq. (10)'s first section defines the hightemperature zone (σ_{High}), a result of band conduction with extended states within the mobility gap in amorphous glasses. The low-temperature zone (σ_{Low}) characterizes the conduction process arising from tunneling between nearby unoccupied sites or hopping of tiny polarons or electrons through localized or defect states at lower temperatures.

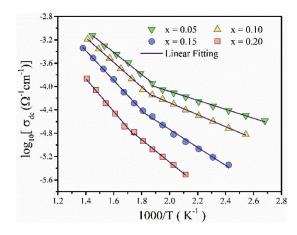


Figure 6. DC Conductivity spectra with reciprocal of temperature

The composition determines pre-exponential factors $\sigma_{\!_{High}}$ and $\sigma_{\!_{Low}}$

At low temperatures within the mobility gap or optical bandgap, conduction involves the hopping of small polarons or charge carriers between localized states, adhering to Mott's variable range hopping (VRH) model (Elliott, 1994).

$$\sigma_{dc} = B \exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right]$$
(11)

and,

$$T_0 = \frac{16\alpha^3}{K_B N(E_{FM})} \tag{12}$$

Mott's VRH model is applicable when localized states exist at the Fermi energy level, and state densities are finite. The Mott's VRH conductivity Eqn. (11-12) is represented, where $N(E_{FM})$ signifies the density of states at the Fermi level, T_0 represents the characteristic temperature, and α^{-1} corresponds to the localization length of the tiny polaron wave function (Biswas et al., 2019b). Figure 7 illustrates the plot of σ_{de} versus $T^{-0.25}$, showing agreement between experimental values and Eq. (11). The density of states at the Fermi level ($N(E_{FM})$) is evaluated using Eq. (12) with a slope from the linear-fit data in Figure and assuming a value of $\alpha^{-1} = 10$ Å for localized states.

To predict temperature-dependent parameters associated with small polaron hopping, such as hopping distance (R_{hop}) and average hopping energy (W_{hop}) , Eqs. (13) and (14) are utilized (Mandal et al., 2023).

$$R_{hop} = \left(\frac{9}{8\pi N(E_{FM})\alpha K_B T}\right)^{1/4}$$
(13)

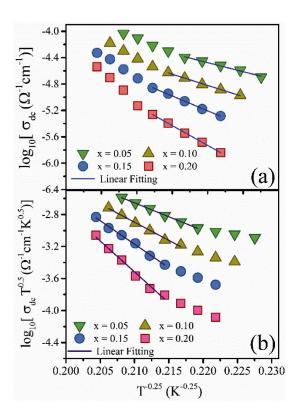


Figure 7. (a) Mott's and (b) Greave's model representation

and,

$$W_{hop} = \frac{3}{4\pi \left(R_{hop}\right)^3 N(E_{FM})} \tag{14}$$

The values of R_{hop} and W_{hop} at a fixed temperature (T = 413 K) are detailed in Table 3. It is observed that $R_{hop}\alpha \ge 1$ and $W_{hop} > K_BT$ and $W_{hop} > K_BT$, prerequisites for the validity of Mott's VRH model, are consistently met across all glassy systems. The results in the Table 3 show that as DC conductivity increases, R_{hop} and W_{hop} values decrease with increasing TiO₂ concentration (x), indicating accelerated conduction due to reduced hopping time and energy requirements between nearby sites.

However, Mott's VRH model is not effectively describing the temperature dependence of σ_{dc} spectra higher than half of the Debye temperature ($\theta_{D/2}$). To account for DC conduction at high temperatures (> $\theta_{D/2}$), Greaves proposed an additional equation (Biswas et al., 2023).

$$\sigma_{dc} T^{1/2} = A' \exp\left[-\left(\frac{T_0'}{T}\right)^{1/4}\right]$$
(15)

and,

$$T_0' = \frac{19.4\alpha^3}{K_B N(E_{FG})}$$
(16)

Parameters	TiO ₂ Content			
	0.05	0.10	0.15	0.20
$E_{\rm Low}~({\rm eV})$	0.42	0.51	0.66	0.79
$E_{\rm High}~({\rm eV})$	1.12	1.24	1.41	1.52
$N(E_{FM})(\times 10^{27} eV^{-1} cm^{-3})$	6.11	5.48	5.03	4.12
$N(E_{FG}) (\times 10^{27} eV^{-1} cm^{-3})$	0.67	0.98	1.12	1.32
R _{Hop} (at 413K) (nm)	3.33	3.65	4.12	4.72
$W_{Hop}(at 473K) (meV)$	0.61	0.76	0.82	0.98

Table 3. Several electrical parameters

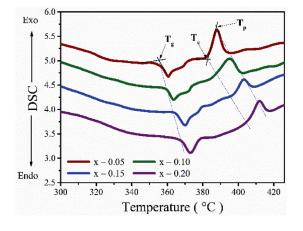


Figure 8. DSC Plot of studied glasses

The Greaves's variable range hopping (VRH) model, represented by equations (15) and (16), is employed to fit σ_{dc} spectra at elevated temperatures. The density of states (DOS) at the Fermi level (N(E_{FG})) is determined using Greaves's VRH model by applying Eq. (15) to the slope of the linear-fit data in the high-temperature region, as depicted by the solid lines in Figure 7(b). The values of N(E_{FM}) and N(E_{FG}) show an decreasing trend with the rising content of TiO₂ (x), as observed in Table 3. This decreasing behavior in N(E_{FM}) and N(E_{FG}) provides insight into the declining σ_{dc} across all glass systems.

3.6 THERMAL STUDY:

Figure 8 shows DSC curves for the studied glasses, confirming homogeneity with one T_g per composition. Exothermic peaks indicate amorphous-crystalline transitions. Table 4 lists measured thermal parameters, revealing a rise in glass transition temperature with increasing Titanium oxide concentration (x).

These curves can be distinguished by their glass transition temperature (T_g) , crystallization temperature (T_c) , and peak crystallization temperature (T_p) . The graph exhibits an endothermic step at the glass transition temperature, with an exothermic second peak resulting from phase change.

Table 4. Obtained values of thermal parameters

x	Т _g (°С)	Т _с (°С)	Т _Р (°С)	$(\Delta T = T_c - T_g) (^{\circ}C)$
0.05	356	380	388	24
0.10	361	387	395	26
0.15	367	396	407	29
0.20	371	403	413	32

The crystallization temperature, Tc, increases with rising Titanium oxide concentration (x), along with T_g and T_p values. The samples demonstrate thermal stability across a wide temperature range, suggesting suitability for high-temperature applications. The higher Titanium content enhances stability against crystallization, evidenced by an increase in (Tc-Tg). Therefore, adding TiO₂ to the glassy matrix increases thermal stability, likely due to higher cross-link density and stretching force constants.

4. CONCLUSIONS

In the current experiment, Glass compositions with the formula $xTiO_2$ -(0.30-x)Bi₂O₃-0.10ZnO-0.60TeO₂ were synthesized, confirming amorphous nature via XRD. Increasing titanium oxide led to higher molar volume (48.21-53.06cc) and lower density (4.18-3.96g/cc). Density and ultrasonic velocities determined longitudinal and shear strains, resulting in Poisson's ratio and elastic moduli. Elastic moduli increased with more titanium oxide, indicating improved elastic properties. Optical absorption spectrum determined bandgap energy, showing structural changes with TiO₂ concentration. Semiconducting behaviour was observed through temperature-dependent DC conductivity. Mott's VRH model explained lowtemperature conduction, while Greaves's VRH model addressed limitations at higher temperatures. Thermal parameters from DSC curve increased with TiO₂ addition, providing insights into complex conductivity mechanisms for potential applications.

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