



Correlative analysis of electrical-structural properties of $60\text{B}_2\text{O}_3\cdot 15\text{ZnO}\cdot x\text{Li}_2\text{O}\cdot (25-x)\text{Bi}_2\text{O}_3$ glass system

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ARTICLE INFO

Keywords:

Oxide glasses
Impedance spectroscopy
Activation energy
Modulus

ABSTRACT

The electrical conductivity of $60\text{B}_2\text{O}_3\cdot 15\text{ZnO}\cdot x\text{Li}_2\text{O}\cdot (25-x)\text{Bi}_2\text{O}_3$ glass system has been measured by complex impedance spectroscopy in the frequency range from 100 Hz to 5 MHz and temperature range 623–723 K with varying Li_2O concentration. Experimentally observed data of ac conductivity is fitted with Jonscher's power law, and conductivity parameters viz. crossover frequency (ω_H), frequency exponent (s), dc conductivity (σ_{dc}), enthalpy of formation (H_f), and migration (H_m) of the Li^+ ion have been estimated. Quantum Mechanical Electron tunnelling theory of conduction mechanism is found applicable in these glasses. At a given temperature, conductivity increases with Li_2O content. The stretch parameter ' β ' is observed to be temperature-dependent, and its value increases with a rise in Li_2O content (β is 0.829 for $x=10$ and 0.928 for $x=25$ at 663 K), which signifies increased structural homogeneity and a smaller distribution of relaxation times. Relaxation time estimated from both electric modulus (τ_M) and impedance (τ_Z) decreases with an increase in Li_2O content. With Li_2O content, experimental values of dc (E_{dc}) and ac (E_a) activation energies of the studied glass system follow similar behaviour as the total concentration of tetrahedral BO_4 units (N_4). An increase in the N_4 fraction signifies a decrease in the activation energy for ionic conductivity.

1. Introduction

Ion-conducting oxide glasses have been investigated extensively owing to their technological utilisation, such as solid-state rechargeable batteries, electrolytes in fuel cells, chemical sensors, thin-film batteries, integrated circuits, and several electrochemical devices [1–5]. Investigation of different properties of glasses, viz., thermal, structural, electrical, etc., has become an important area of interest for many researchers because the required material should possess structural stability along with high ionic conductivity [6]. However, these two properties usually preclude each other. Contrary to silicate and phosphate glasses, borate glasses are structurally more complicated due to the presence of two types of boron-oxygen coordination, viz., trigonal planar BO_3 and tetrahedral BO_4 structural units [7]. B_2O_3 glass comprises corner-shared trigonal BO_3 units; a significant portion of these units forms three-membered boroxol rings [8]. Contrary to silicate glasses, the addition of alkali modifiers (Li_2O , Na_2O , K_2O , etc.) to B_2O_3 -based glasses not only creates non-bridging oxygens (NBOs) but

also leads to charge stabilization by the conversion of trigonal BO_3 structural units to tetrahedral BO_4 units, which enhances connectivity in glass matrix, or create NBOs by rupturing the linkage between two trigonal BO_3 units [8–10]. Also, borate glasses containing Bi_2O_3 show large polarizability, high refractive index [11], radiation shielding behaviour [12], and have potential applications in the fields of mechanical and thermal sensors, glass-ceramics, layers for electronic and devices, and IR-transmitting windows [13]. Additionally, Bi_2O_3 glasses substituted with Na, Li, and K alkali ions play a salient role in optical fibres, microelectronics, and optics-based applications [2,14–16]. Lithium ions, due to their highly electropositive character, lighter weight, and smaller size, give rise to high operational voltage windows and high energy density in micro-batteries [2]. Numerous studies have been done on binary lithium-doped borate glasses [17–19]. In Bismuth oxide-based glasses, Li_2O acts as a feasible solid-state electrolyte, intensifying electrical conductivity and making them the appropriate applicants in high-energy-density batteries and sensors [20,21]. So, here, adding zinc oxide to the ternary glass composition of Lithium

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<https://doi.org/10.1016/j.jnoncrysol.2025.123854>

Received 23 July 2025; Received in revised form 30 October 2025; Accepted 31 October 2025

Available online 8 November 2025

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Bismuth Borate could reform the properties remarkably by providing higher elastic moduli and fracture toughness. Also, the inclusion of zinc oxide leads to the creation of BiO_6 octahedral units as a result of the replacement of the B-O bond by the Bi-O bond. Zinc oxide is a multifunctional semiconductor with a broad bandgap, whose inclusion in borate glasses reduces crystallisation, lowers the melting point [22], enhances chemical durability, and makes them thermally more stable and useful in many electronic and optical devices. So, to fully comprehend the ionic conductivity in the glass network, it is necessary to examine a broad range of compositions and correlate structural studies and electrical conductivity measurements to learn more about how the composition and temperature of the glass network alter it. Numerous studies have shown that bismuth-based glasses accommodating Li^+ ions have excellent ionic conductivity and are suitable for utilization as vitreous ion conductors [23]. There are many reports on the structural and electrical properties of ternary [2,24–28] and very few on quaternary [29–31] bismuth borate glasses.

The incorporation of higher concentrations of borate, which are rarely reported, is what makes this work novel. Additionally, considering the applicability of bismuth borate glasses for technological advancements, a systematic study of ion transport properties of different compositions of $60\text{B}_2\text{O}_3.15\text{ZnO}.x\text{Li}_2\text{O}.(25-x)\text{Bi}_2\text{O}_3$ glass system is, therefore, called for. The detailed investigation of physical, structural, and optical properties has been reported in M. Bala *et al.*'s earlier work [32]. This paper presents a systematic investigation of ion transport characteristics of lithium-modified bismuth zinc borate glass system over a wide composition range by taking temperature and frequency-dependent conductivities and correlating the Li^+ transport to structural changes in the glass network. We will carry out the study of dielectric properties in terms of ac conductivity, impedance spectroscopy, and modulus formalism, which helps assess the conduction mechanism in glasses and suggest their possible usability in solid electrolytes, electrochromic and device applications.

2. Experimental details

Glasses having compositions $60\text{B}_2\text{O}_3.15\text{ZnO}.x\text{Li}_2\text{O}.(25-x)\text{Bi}_2\text{O}_3$ (where x is varied from 5 to 25 mol % in steps of 5) had been synthesized by melt-quenching methodology using AR-grade chemicals, namely Bi_2O_3 , H_3BO_3 , ZnO and Li_2CO_3 . The complete synthesis process is reported in our previous communication [32]. The sample names given to the different glass compositions are listed in Table 1. Properly annealed glass samples were lapped on two opposite faces and cut into a rectangular shape with a thickness of about 1 mm. A thin coating of silver paste is applied on the as-prepared cuboidal-shaped samples, which serves as electrode material for electrical measurements. Dielectric loss and capacitance were recorded via the Wayne Kerr 6500B impedance analyzer within the frequency region 100 Hz to 5 MHz and different temperature values varying from 623 K to 723 K in steps of 10 K. Linear and nonlinear curve-fitting modules of OriginPro and Z-view software were used to fit the experimental data obtained from Impedance spectroscopy.

Table 1

Assignment of Sample names to the prepared glass system $60\text{B}_2\text{O}_3.15\text{ZnO}.x\text{Li}_2\text{O}.(25-x)\text{Bi}_2\text{O}_3$, where $x = 5, 10, 15, 20$, and 25 mol %.

Glass composition	Sample name
$60\text{B}_2\text{O}_3.15\text{ZnO}.5\text{Li}_2\text{O}.20\text{Bi}_2\text{O}_3$	BZL-5
$60\text{B}_2\text{O}_3.15\text{ZnO}.10\text{Li}_2\text{O}.15\text{Bi}_2\text{O}_3$	BZL-10
$60\text{B}_2\text{O}_3.15\text{ZnO}.15\text{Li}_2\text{O}.10\text{Bi}_2\text{O}_3$	BZL-15
$60\text{B}_2\text{O}_3.15\text{ZnO}.20\text{Li}_2\text{O}.5\text{Bi}_2\text{O}_3$	BZL-20
$60\text{B}_2\text{O}_3.15\text{ZnO}.25\text{Li}_2\text{O}$	BZL-25

3. Results and discussion

To study ion dynamics, various dielectric parameters such as the real component of ac conductivity (σ'), dielectric constant's real (ϵ') and imaginary (ϵ'') elements, impedance's real (Z') and imaginary (Z'') elements, and real (M') and imaginary (M'') elements of electric moduli are computed from the as-measured values of dielectric loss ($\tan\delta$) and capacitance (C) using different relevant relationships [3,33,34]. AC conductivity and other electrical parameters of the BZL-5 glass sample are below the resolution of our instrument; therefore, the results of this sample are not reported.

3.1. Alternating conductivity (AC) analysis

Electrical conductivity is a widely used and accepted physical property for understanding the ion dynamics and transport phenomenon in non-crystalline materials like glass [35–37]. The change of real component of the ac conductivity spectra, $\sigma'(\omega)$, covering all the glass specimens with varying frequencies at $T=693$ K, has been represented in Fig. 1. As observed from the figure, similar frequency dependency is exhibited by all glass compositions. Also, with increasing Li_2O concentration, an appreciable increment in frequency-dependent conductivity ($\sigma'(\omega)$) is noted at any particular temperature for the studied frequency span. It's worth noting that at lower frequencies, $\sigma'(\omega)$ is nearly frequency independent and is in line with dc conductivity (σ_{dc}), while it shows dispersion behavior at high frequencies [20,38]. The lower frequency domain is called the plateau region, while the higher frequency region is called the dispersion region. Frequency-dependent conductivity for BZL-20 has been plotted in Fig. 2, and it is observed that with increasing temperature, dispersion starts at a bit higher frequency, inducing a drop in the width of the dispersion region. The transition of frequency-independent dc conductivity regime to frequency-dependent ac conductivity regime demonstrates the inception of the relaxation phenomenon. It is acknowledged that the plateau region's width increases with Li_2O content for the studied set of glasses (Fig. 1) and with the rise in temperature for a particular glass composition (Fig. 2). Consequently, higher frequencies reflect the dispersion zone with increasing temperature and Li_2O content. It's interesting to mention that ionic (dc) conductivity is enhanced by 3 orders of magnitude ($\sim 10^{-7}$ S/cm for BZL-10 and $\sim 10^{-4}$ S/cm for BZL-25) at 713 K as Li_2O is varied from 10 to 25 mol %. These good values of conductivity make them a promising material for applications as solid electrolytes, electrochemical sensors, and electrochromic devices, and analogous findings were

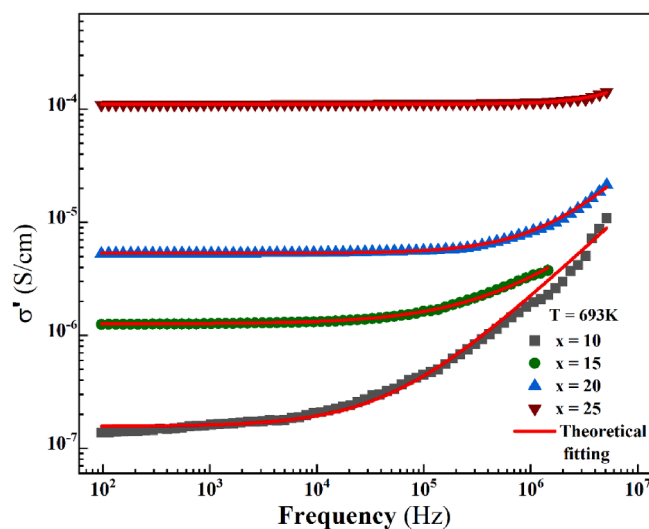


Fig. 1. Composition-dependent variation in σ' vs. frequency for BZL glasses at 693 K temperature.

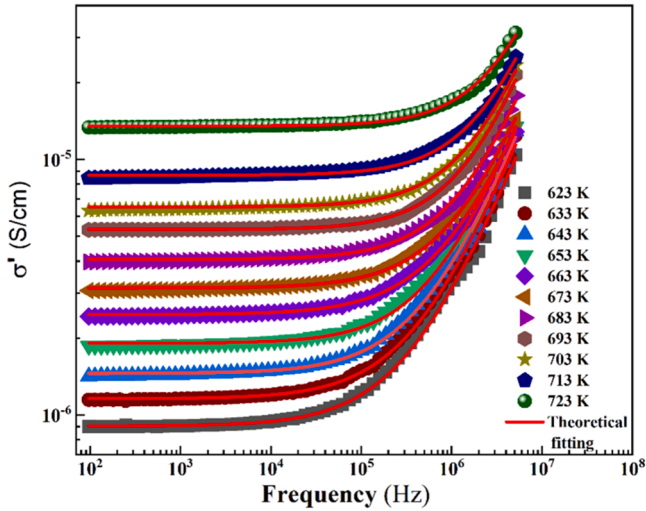


Fig. 2. Fitted ac conductivity (σ') isotherms of BZL-20 sample using Eq. (1).

reported earlier for many other glass systems, which is consistent with previously reported glass systems [29,34,39–41].

The ac conductivity ($\sigma'(\omega)$) corresponding to hopping charges obeys Jonscher's power law of conductivity given by the relation in which ω_H denotes the crossover frequency separating dc plateau region from the dispersive conduction region, s signifies the exponent of frequency ($0 < s < 1$), and σ_{dc} is dc conductivity [41–45].

$$\sigma'(\omega) = \sigma_{dc} \left[1 + \left(\frac{\omega}{\omega_H} \right)^s \right] \quad (1)$$

The corresponding values of the above-mentioned parameters (ω_H , s , and σ_{dc}) are evaluated by fitting the experimental data of $\sigma'(\omega)$ at distinct temperature values with Jonscher's power law (Eq. (1)) as illustrated in Fig. 2, with best-fit parameter (R^2) lying within the span 0.9853–0.9985 and least square fit error factor (χ^2) within 1.14×10^{-15} – 2.938×10^{-16} . All the prepared glass specimens comply with the universal Jonscher power law, suggesting that the hopping mechanism is accountable for AC conduction [39].

As stated by Mundy and Jain [46], when the conduction happens by defect mechanism, few percentage (n) of the total number of ions (N) are active at a particular time, then

$$n = N \left(-\frac{G_f}{kT} \right) = N \exp \left(\frac{S_f}{k} \right) \times \exp \left(-\frac{H_f}{kT} \right) \quad (2)$$

Here, H_f , G_f , and S_f represent enthalpy, free energy, and entropy, respectively, to dissociate the cation from its initial position to a centre that compensates charge. The DC conductivity and crossover frequency have been provided by [46]

$$\sigma_{dc} = \frac{NZ^2e^2d^2\gamma\omega_o}{kT} \exp \left(\frac{S_f + S_m}{k} \right) \times \exp \left(-\frac{H_f + H_m}{kT} \right) \quad (3)$$

and

$$\omega_H = \omega_o \exp \left(\frac{S_m}{k} \right) \times \exp \left(-\frac{H_m}{kT} \right) \quad (4)$$

where d represents jump distance, γ is a constant that includes correlation and geometrical factors. ω_o , H_m , and S_m denote attempt frequency, enthalpy, and entropy of migration, respectively. Reorganisation of Eqs. (3) and (4) give a link between ω_H and σ_{dc} as

$$\sigma_{dc} = \frac{NZ^2e^2d^2\gamma\omega_H}{kT} \exp \left(\frac{S_f}{k} \right) \times \exp \left(-\frac{H_f}{kT} \right) \quad (5)$$

In the above expression, at a fixed temperature value, σ_{dc} is in direct

relation with ω_H , which is in concordance with the Barton-Nakajima-Namikawa (BNN) relation [42]

$$\sigma_{dc} = p\epsilon_o\Delta\epsilon\omega_m \quad (6)$$

where p is the constant value with order 1, $\Delta\epsilon = \epsilon_o - \epsilon_\infty$ and depends on temperature, ϵ_o represents the electrical permittivity of free space, ϵ_∞ denotes dielectric constant at higher frequency, and ω_m signifies peak frequency of dielectric loss. It's quite evident from Eqs. (3) and (4), that slope values of $\ln(\sigma_{dc}^*T)$ and $\ln(\omega_H)$ vs. $1/T$ plots shall be $H_f + H_m$ and H_m , respectively, which are estimated using linear fitting with a linearity of >0.99 for all prepared glass specimens (Fig. 3 and Fig. 4). The calculated values $H_f + H_m$ and H_m have been given in Table 2.

Further, the conduction mechanism present in the studied glasses is determined by the temperature dependence of frequency exponent ' s '. Several models have been used to find the conduction mechanism of glassy materials based on the variation of the parameter ' s ' with temperature. These models include charge carrier hopping over a barrier (CBH), Quantum mechanical electron tunnelling (QMT) and large polaron tunnelling with overlapping (OLPT) [47,48]. The determined values of ' s ' by fitting of ac conductivity ($\sigma'(\omega)$) data using Eq. (1), are plotted as a function of temperature (Fig. 5). ' s ' values are observed in the range 0.7311–0.9997. As observed from Fig. 5, for all the studied glass samples, ' s ' values remain nearly constant over the entire temperature range, suggesting the presence of QMT conduction mechanism [39,49].

3.2. Impedance formulation

Impedance spectroscopy (IS) is a versatile tool for investigating ion dynamics in different materials, such as glasses, electrolytes, and ceramic materials, by identifying and separating different contributions to the electric and dielectric response of the materials. Any change in ion dynamics is characterized by the variation in complex spectra of conductivity, impedance, electric modulus, and permittivity parameters. Evaluation of these spectra helps to identify and understand the conduction mechanism.

The values of the real (Z') and imaginary (Z'') components of impedance at various temperatures as a frequency function were evaluated using permittivity values. The complex impedance or Nyquist plots (graph between $-Z''$ versus Z') are semicircular arcs in all glass samples. A typical Nyquist plot for BZL-20 sample is shown in Fig. 6. However, in BZL-25 glass specimen, in low-frequency domain and at some temperatures, a small straight spike follows the semicircular arc. The presence of the spike may be because of electrode polarization

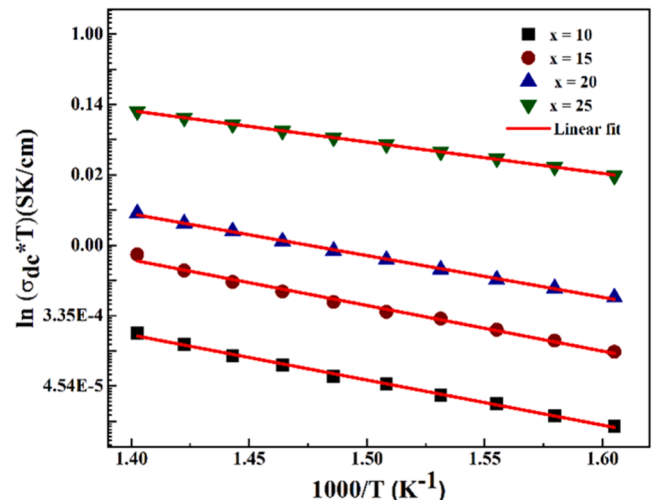


Fig. 3. Linear fit $\ln(\sigma_{dc}^*T)$ vs. $1/T$ of BZL glass specimens.

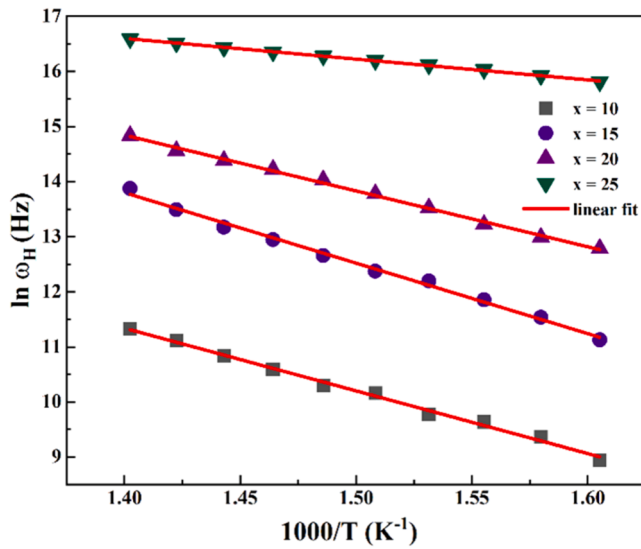


Fig. 4. Linear fit $\ln(\omega_H)$ versus $1/T$ of BZL glasses.

Table 2

Enthalpy (H_f) and migration enthalpy (H_m) of BZL glasses for different x values.

Enthalpy	BZL-10	BZL-15	BZL-20	BZL-25
$H_f + H_m$ (eV) (± 0.0001 eV)	1.1032	1.1171	1.0194	0.7671
H_m (eV) (± 0.0001)	0.9811	1.1092	0.8735	0.4349
H_f (eV) (± 0.0001)	0.1221	0.0079	0.1459	0.3321

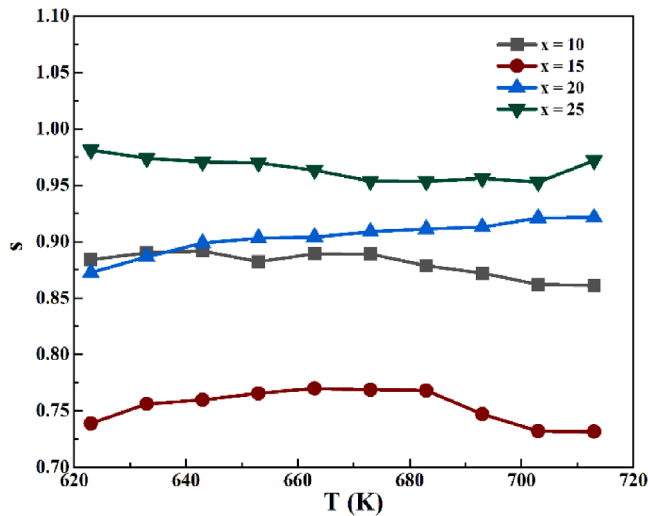


Fig. 5. Frequency exponent value (s) variation with temperature for different BZL glass compositions.

caused by diffusion of ions in the electrodes, which is due to accumulation of Li^+ ions at the electrode-glass interface [4,44]. In all glass compositions, $-Z''$ versus Z' semicircular arcs are depressed, and their centres lie below the Z' axis, thereby suggesting non-Debye type relaxation [50,51]. Ideally, for a solid-state electrolyte, the impedance plot should be a semicircle with centre at real axis (Z') and fit to an electrical equivalent circuit with a parallel combination of capacitor and resistance. However, in the presently studied glasses, this semicircle is depressed. Therefore, to incorporate the effect of this depression of a semicircular arc, a constant phase element (CPE) is kept in the equivalent circuit instead of capacitance. An idealized equivalent electrical circuit model consisting of R_b and CPE in parallel, as shown in Fig. 6, is

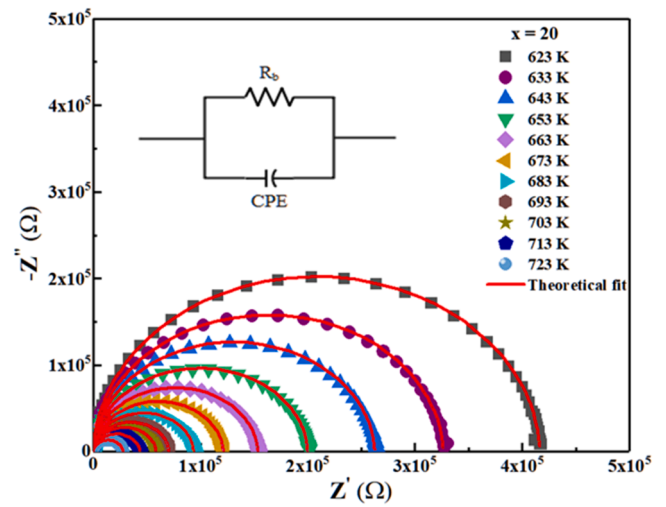


Fig. 6. Nyquist plots for BZL-20 glass specimen at distinct temperatures. Solid lines and symbols represent the R-CPE model fit and experimental data, respectively.

used in impedance analysis of the prepared glasses. The total complex impedance (Z^*) is given as

$$Z^* = \text{Re}Z^* + j\text{Im}Z^* = Z' + jZ'' = \left[\frac{1}{R_b} + \frac{1}{Z_{\text{CPE}}} \right] \quad (7)$$

Here the following relation defines the impedance of CPE [50]

$$Z_{\text{CPE}}^* = \frac{1}{A_0(j\omega)^\alpha} \quad (8)$$

where A_0 is some constant which is frequency-independent in $\text{Fs}^{\alpha-1}$ [50], ($\omega = 2\pi f$, f being frequency) is the angular frequency, j ($j^2 = -1$) is the imaginary unit, and α is a dimensionless parameter having values between 0 and 1. ' α ' determines the degree of deviation from a precise semicircle. For $\alpha = 1$, Z_{CPE}^* gives the impedance value corresponding to a perfect capacitor and $A_0 = C$ in Eq. (8).

The experimental impedance data are fitted via the proposed equivalent circuit using Z-view software. Fig. 6 represents the fitting of impedance data (experimental) with R-CPE model for BZL-20; a very good agreement is obtained between the theoretical fitted and experimental data. The equivalent circuit parameter values, viz. phase angle (α), capacitance (C), and resistance (R_b), computed from theoretical fitting using R-CPE model are listed in Table 3. It is clearly visible (in Table 3) that $\alpha < 1$ for each glass composition studied at different temperatures, implying the existence of a “non-Debye relaxation mechanism” in these glasses [52–56]. The presence of a single semicircle at all temperatures indicates the presence of a single relaxation mechanism [57]. In the understudy glass specimens, with rising temperature, the diameter of semi-circular arc decreases, which suggests a decline in bulk resistance (R_b) and enhancement in dc conductivity. The dc conductivity (σ_{dc}) values and relaxation time ' $\tau_{Z'}$ ' are determined using the following relations [58]

$$\sigma_{dc} = \frac{l}{R_b A} \quad (9)$$

$$\tau_{Z'} = 2\pi R_b C \quad (10)$$

where R_b , C , A , and l are the bulk resistance, capacitance, area, and thickness of the glass sample, respectively. Variation of dc conductivity (σ_{dc}) with reciprocal temperature is presented in Fig. 7 and observed to follow the Arrhenius behaviour via relation [41]

Table 3

Equivalent circuit parameters resistance (R), capacitance (C), and phase angle (α) obtained from R-CPE model fitting of experimental impedance data of BZL glass system.

T (K)	BZL-10			BZL-15			BZL-20			BZL-25		
	R (k Ω)	C (pF)	α	R (k Ω)	C(pF)	α	R (k Ω)	C(pF)	α	R (k Ω)	C(pF)	α
623	15,911	61.70	0.989	1375.5	72.15	0.979	416.4	70.22	0.981	5.152	127.6	0.947
633	12,270	64.43	0.986	1035.9	73.48	0.979	326.4	71.80	0.980	4.056	129.0	0.946
643	8457.2	61.10	0.989	778.16	75.19	0.997	262.6	74.30	0.977	3.230	131.0	0.944
653	7216.3	63.48	0.987	561.56	73.76	0.979	200.0	74.83	0.976	2.708	133.0	0.943
663	5185.3	66.33	0.984	475.23	75.49	0.978	153.6	76.47	0.975	2.234	136.7	0.940
673	4315.5	65.92	0.984	364.96	76.30	0.977	121.5	80.14	0.972	1.873	141.0	0.938
683	3153.0	66.79	0.984	276.84	77.05	0.977	93.70	80.50	0.972	1.572	152.1	0.932
693	2472.1	70.16	0.981	212.74	78.37	0.976	70.70	76.40	0.976	1.324	162.1	0.929
703	1841.0	71.49	0.979	154.76	77.60	0.977	58.76	86.69	0.966	1.115	185.1	0.918
713	1380.7	79.60	0.969	100.08	85.00	0.971	43.87	99.08	0.956	0.948	231.3	0.907
723	886.1	75.00	0.976	62.329	79.77	0.976	27.48	99.86	0.960	0.768	261.0	0.903

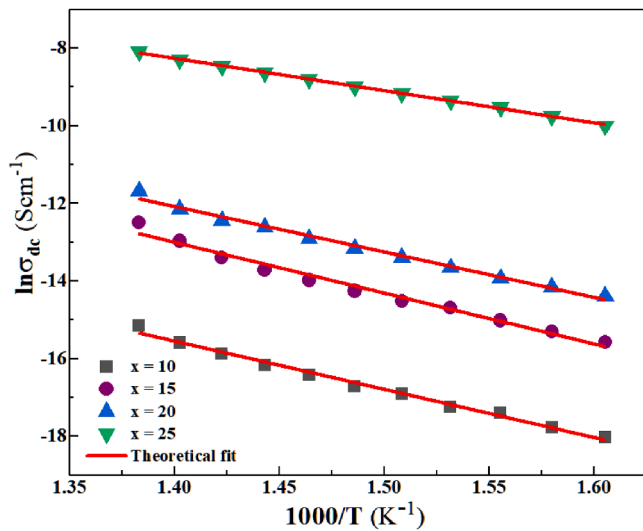


Fig. 7. The plot of $\ln \sigma_{dc}$ vs $1000/T$ for different BZL glass compositions. The solid lines represent the linear fit using Eq. (4.12), and symbols represent the experimental data.

$$\sigma_{dc} = \sigma_0 \exp\left(-\frac{E_{dc}}{k_B T}\right) \quad (11)$$

where k_B is the Boltzmann constant, E_{dc} is the activation energy, and σ_0 is the pre-exponential factor, which represents conductivity at a very high temperature. The linear fitting of experimental data of $\ln \sigma_{dc}$ versus $1000/T$ plots has been performed and presented in Fig. 7. The values of goodness of fit parameters (R^2) are in the range 0.989 - 0.999, thereby confirming the Arrhenius behaviour of dc conductivity of presently studied glass system. The activation energy (E_{dc}) has been calculated from the slopes of the linear fit of respective experimental data of $\ln \sigma_{dc}$.

Table 4

Relaxation time of electric impedance (τ_Z), electric modulus' relaxation time ($\tau_{M''}$), dc activation energy of impedance (E_{dc}), impedance's ac activation energy (E_z), electric modulus' activation energy (E_R), fraction of BO_4^- units (N_4) and glass transition temperature (T_g) for different BZL glass compositions.

Parameter	BZL-10	BZL-15	BZL-20	BZL-25
τ_Z (μ s) at 703 K	826.5	75.4	32.0	1.29
$\tau_{M''}$ (μ s) at 703 K	101.9	8.3	3.05	0.005
E_{dc} (eV)	1.071	1.130	1.010	0.718
E_z (eV)	0.983	1.084	0.885	0.459
E_R (eV)	1.229	1.142	1.083	0.735
N_4	0.359	0.345	0.387	0.481
T_g (K)	746.80	745.15	748.14	751.41

versus $1000/T$ and listed in Table 4.

The frequency-dependent spectrum (Fig. 8) of impedance's real component (Z') of BZL-20 at various temperatures shows the usual trend and a good fit with the R-CPE model. For BZL-20, the alterations of normalized Z' , i.e., Z'/Z'_{max} with frequency at various temperatures are shown in Fig. 9. It is clearly visible from the data shown in Fig. 8 and Fig. 9 that there are two plateau regions, one at lower frequency domain while another at higher frequency domain. At a certain specific temperature, Z' value is more at a low-frequency range compared to its values at a high-frequency span, which is an indicator of space charge polarization of the material [50]. For every glass specimen with rising temperature, Z'_{max} , i.e., the utmost value of impedance's real component in the low-frequency domain, was found to decrease, but the plateau domain's width verifies that an upsurge in temperature induces a rise in the dc contribution. The Z' spectra for different temperatures finally merge at higher frequencies. This merging of the real component of impedance in high-frequency regions implies the liberation of space charge, thereby resulting in the decline of the material's barrier characteristics [50]. Constant values of Z' in the low region at a fixed temperature indicate dc conduction, and the decline in Z' values with the rise in temperature signifies a negative temperature coefficient similar to semiconductors. In this glass system, with increasing Li_2O content, the merging point frequency corresponding to Z' at different temperatures is found to shift to higher frequencies, which indicates that dc conduction increases whereas frequency-dependent ac conduction decreases. Further, at a specific temperature for different glass compositions with

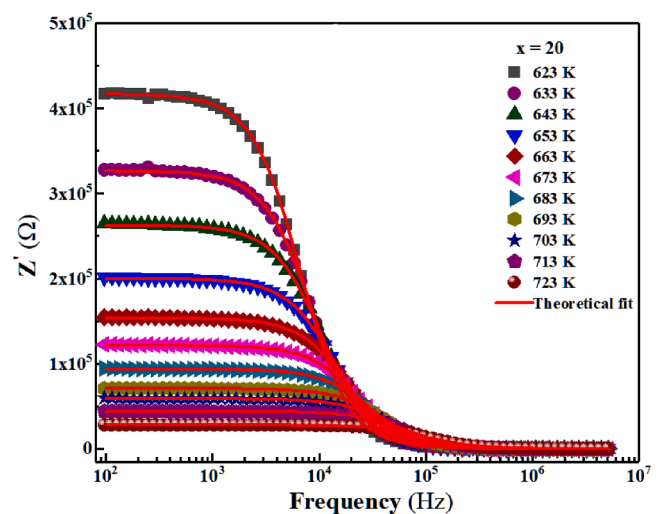


Fig. 8. Fitted frequency-dependent spectra of impedance's real component (Z') for BZL-20 glass specimen at different temperatures with R-CPE model.

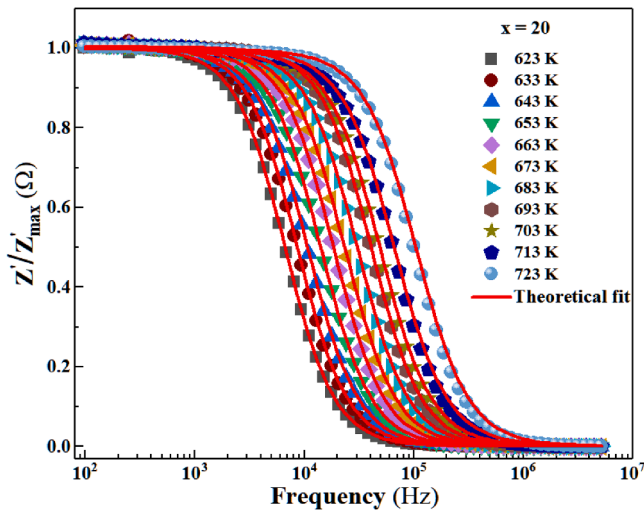


Fig. 9. Normalized Z' ($Z'/Z'_{\max}$) vs frequency for BZL-20 at different temperatures.

an increment in Li_2O concentration, Z' value was observed to decrease, whereas the width of the low-frequency plateau increases, thereby indicating an increase in dc conduction.

Fig. 10 shows the temperature dependence of the impedance's imaginary component (Z'') with the frequency for BZL-20 glass. Z'' shows a usual trend and a good fit with the R-CPE model. The alteration of normalized Z'' , i.e. $Z''/Z''_{\max}$ with frequency for BZL-20 glass sample at various temperatures is presented in Fig. 11. Z'' spectra of other glass samples also exhibited similar temperature dependence. In Z'' spectra of all glasses, one prominent peak is observed for each studied temperature. This peak's emergence in the spectrum implies the onset of electrical relaxation and the existence of the single relaxation phenomenon in every glass specimen. With the rising temperature, the peak of normalized Z'' spectra shifts towards higher frequencies, while peak height ($Z''_{\max}$) decreases, accompanied by peak broadening. The asymmetric broadening of the peaks suggests the presence of electrical processes in the studied glasses with a spread of relaxation time [50], and hence, the electrical relaxation phenomenon in the studied glasses is temperature-dependent. Furthermore, the merging of Z'' spectra in the low-frequency domain is seen in BZL-25, which indicates the noticeable accumulation of space charge in these samples as compared to BZL-10, BZL-15, and BZL-20 glasses.

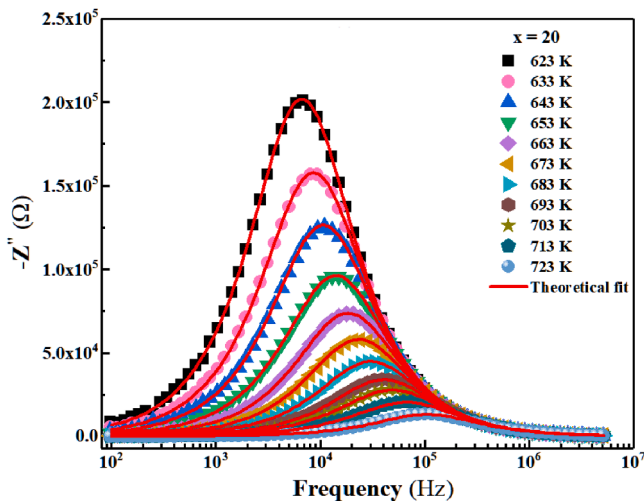


Fig. 10. Fitting of frequency spectra of Z'' using R-CPE model of BZL-20 at different temperatures.

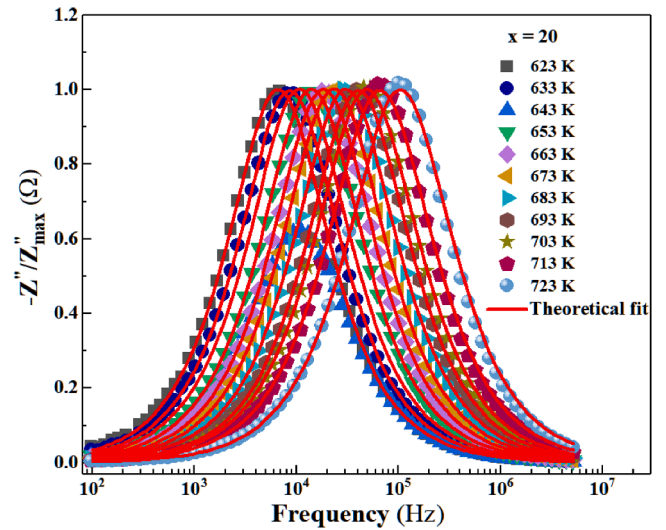


Fig. 11. Normalized Z'' ($Z''/Z''_{\max}$) vs frequency for BZL-20 at different temperatures.

The relaxation frequency of Z'' spectra, i.e., peak frequency (f_p) for different glass samples are noted at different temperatures, and it is noticed to shift towards greater frequencies, which signifies a thermally activated mechanism of conduction in the understudy glass specimens. The peak frequency (f_p) satisfies the relation

$$2\pi f_p \tau_{Z''} = 1 \quad (12)$$

The values of relaxation time $\tau_{Z''}$ evaluated from Eq. (12) lie in the range of 0.019 μs to 0.443 ms and are observed to follow the Arrhenius behaviour via relation

$$\tau_{Z''} = \tau_0 \exp\left(\frac{E_z}{k_B T}\right) \quad (13)$$

where E_z represents activation energy for ac conduction. In the presently studied set of glasses, dc and ac conductivities change monotonically with temperature which indicates that charge carriers are thermally activated [40,50]. This fact is ascertained by Arrhenius type temperature dependency of $\tau_{Z''}$. The variation of $\ln \tau_{Z''}$ versus $1000/T$ (Fig. 12) for different glasses is fitted with linear fit module and goodness of fitting parameter (R^2) is attained in the range 0.973 - 0.991. The values of E_z are

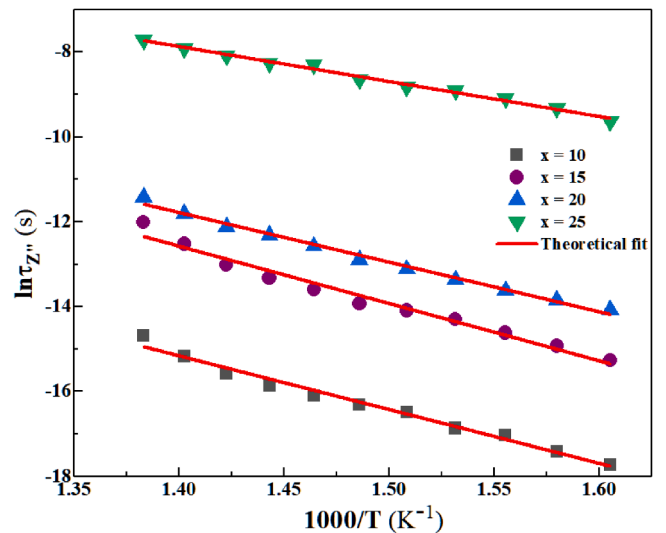


Fig. 12. Plot of $\ln(\tau)$ vs. $1000/T$ for distinct $60\text{B}_2\text{O}_3.15\text{ZnO}.x\text{Li}_2\text{O}.(25-x)\text{Bi}_2\text{O}_3$ glass compositions.

estimated from the slopes obtained from the linear fitting of $\ln \tau_Z''$ vs. $1000/T$ graph (Fig. 12) and listed in Table 4.

The values of both activation energies E_{dc} and E_z (listed in Table 4) exhibit similar trends with increased Li_2O amount. With an increase in Li_2O amount from 10 mol % to 15 mol %, the activation energies are found to increase; however, a further increase in Li_2O amount causes a decline in activation energies. This anomalous behavior in activation energy might be ascribed to structural alterations in the glass network on substitution of Bi_2O_3 by Li_2O . The structural studies of the understudied glass system have been reported in Manju *et al.*'s earlier work [32]; the values of fraction of BO_4^- units (N_4) acquired from structural analysis are given in Table 4. It is noted that, up to $x=15$, N_4 initially decreases with an increase in Li_2O content and then increases on further addition of Li_2O . Pursuant to the Anderson-Stuart model [59], for ion-conducting materials, the activation energy comprises two terms: first, binding or creation energy H_f , representing the energy required for creating a mobile charge carrier in opposition to Coulombian potential energy amongst the negatively charged hosting units (BO_4^-) and cation (Li^+ ion), second, the migration energy (H_m), that is the energy required for distorting the glass network to create a "doorway" through which cation (Li^+ ion) can diffuse to new site. The Li^+ ion induced expansion of the network skeleton would lead to lowering of the migration energy (H_m) (as reported in the Table 2) of the activation energy and the formation of the pathways, in which the cation may coordinate with the oxygens of the network, leading to a lowering of the binding energy (H_f). Further, Montouillout *et al.* [1,17,19] reported that, for low alkali content, due to the small concentration of the BO_4^- units, the distance between the BO_4^- sites is long; consequently, the activation energy, mainly due to the migration energy (H_m), is high. With increasing Li_2O content, the increase in BO_4^- units leads to shortened distances between the BO_4^- sites, resulting in a decrease in the migration energy [1]. In the studied glasses, the changes in the activation energy (E_{dc}) follow a similar behaviour as the total concentration of tetrahedral BO_4 units (N_4) in the glass structure and are plotted in Fig. 13. The increase in N_4 fraction signifies a decrease in the activation energy for ionic conductivity and vice versa.

The data of prepared glasses have been compared with a Li-free Bismuth Zinc Borate glass [60] for thermal, structural and electrical properties. The prepared glasses exhibit a higher glass transition temperature, as reported in our earlier communication [32], compared to Li-free glasses, indicating greater strength or rigidity of the glasses. Further, all Li-free glasses show crystallization peaks in the temperature range 410°C - 510°C , while in the presently studied glass series, none of the sample except $x = 25\text{mol \%}$ ($T_C = 670^\circ\text{C}$) shows crystallization peak. This shows higher thermal stability of the prepared glasses compared to

Li-free glasses. The dc activation energy ' E_{dc} ' values are lower (1.130 - 0.718 eV) for studied glasses as compared to Li-free glasses ' E_{dc} ' values (1.22 - 1.30 eV).

3.3. Electric modulus formulation

Complex electric modulus (M^*) is a powerful tool for investigating the dielectric behavior of insulating materials like glass, mainly at sufficiently high temperatures, where the exceptionally high complex permittivity (ϵ^*) is caused by carrier transport and electrode polarization [61,62]. Electrode polarization is due to the buildup of charges near the electrodes. Such electrode polarization masks the bulk relaxation process and makes it difficult to examine its behavior [61,63]. So, to investigate the existence of inherent dielectric relaxation effects in the studied material, electric modulus formalism is adopted in which such electrode effects are eliminated on an intrinsic dipole. Macedo *et al.* presented the electric modulus formalism, and It is implemented to comprehend the phenomenon of space charge relaxation [64]. In dielectric materials, the electric field relaxation in a given material is represented by electric modulus at fixed values of electric displacement. The complex part of electric modulus (M^*) is connected to complex permittivity (ϵ^*) via [42]

$$M^* = \frac{1}{\epsilon^*} \quad (14)$$

and

$$M^* = M' + iM'' = \frac{\epsilon'}{(\epsilon')^2 + (\epsilon'')^2} + i \frac{\epsilon''}{(\epsilon')^2 + (\epsilon'')^2} \quad (15)$$

where ϵ' , ϵ'' and M' , M'' denote corresponding real and imaginary component of dielectric constant and electric moduli, respectively. M' spectrum's change with frequency (Fig. 14) at different temperatures exhibits the general trend as reported by many authors in amorphous materials [5,29,42,43]. In low-frequency regions, a very low value of M' close to zero is observed at all temperatures under investigation, signifying the dominance of dielectric relaxation behavior due to electrode polarization. M' approaches to the maximum value, i.e., M_∞ at the frequencies $\sim 10^6$, may be ascribed to space charge relaxation process. For all glass samples M_∞ value is observed to drop as temperature rises.

The energy loss exhibited by a dielectric material influenced by an applied electric field concerns the imaginary part of the electric modulus (M''). It (M'') may be articulated using the Fourier transform of $\phi(t)$ (relaxation function giving the electric field's time evolution in the

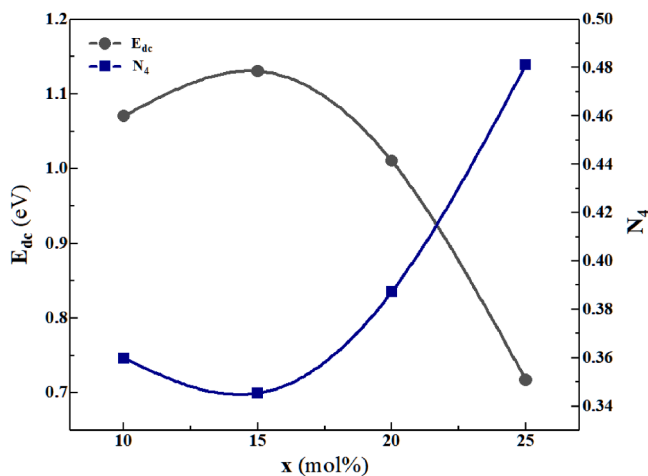


Fig. 13. Compositional variation of dc activation energy (E_{dc}) and fraction of BO_4^- units (N_4) for BZL glass system.

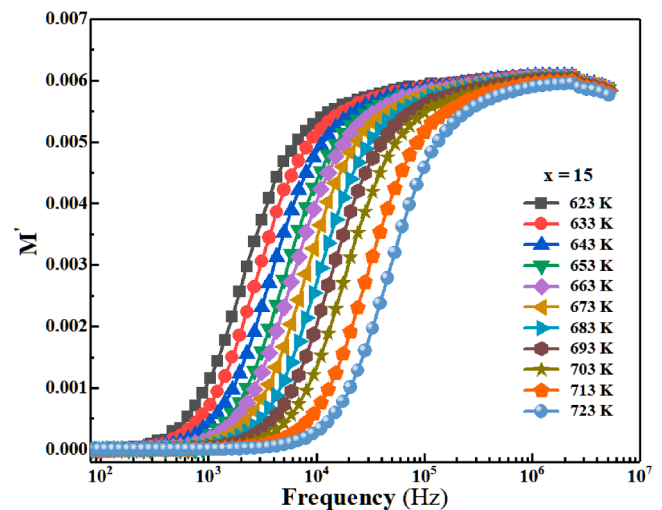


Fig. 14. Real component of electric modulus (M') as a function of frequency for BZL-15 sample at various temperatures.

material), expressed as [42]

$$M'' = M_{\infty} \left\{ 1 - \int_0^{\infty} \exp(-\omega t) \left(\frac{d\varphi}{dt} \right) dt \right\} \quad (16)$$

here, $\varphi(t)$ is generally considered as the Kohlrausch-Williams-Watts (KWW) function in which stretched exponent β (where $0 < \beta \leq 1$) represents a point of deviation from Debye-type relaxation [29] and τ_m denotes the relaxation time corresponding to a conductivity [42]

$$\varphi(t) = \exp \left[- \left(\frac{t}{\tau_m} \right)^{\beta} \right] \quad (17)$$

The values of β can be estimated from the fitting of experimental data with Eq. (16) and Eq. (17), but it's always advantageous to keep a minimum number of modifiable variables during fitting. Adopting this strategy, the electric modulus behavior in the currently presented glass specimens is restructured in terms of the modified-KWW function introduced by Bergman [65]. Imaginary component of electric modulus (M'') in this formulation is demonstrated as

$$M'' = \frac{M''_{\max}}{(1 - \beta) + \frac{\beta}{1 + \beta} \left[\beta \left(\frac{f_{\max}}{f} \right) + \left(\frac{f}{f_{\max}} \right)^{\beta} \right]} \quad (18)$$

where $M''_{\max}$ is peak value of M'' and $f_{\max}$ is peak frequency, i.e., at which M'' reaches its maximum value. Experimental data of M'' at various temperatures for different glasses are fitted theoretically via Eq. (18), and it gives a very good fit. A typical fitting for BZL-25 sample is portrayed in Fig. 15. The fitting parameters $f_{\max}$ and β were evaluated from fitted data. The peak in M'' spectra shifts to larger frequencies with an upsurge in temperature, thereby suggesting the presence of a temperature-dependent relaxing mechanism in the glass samples under study. The shift detected in peak frequency with an increase in temperature here suggests that electrode polarization effects can be minimised while examining the electrical behaviour of these glassy materials. The region of frequency spectrum below the peak frequency ($f < f_{\max}$) is the region where conduction takes place due to movement of Li^+ ions over long distances (DC conduction) and in the frequency spectrum above the peak ($f > f_{\max}$), the motion of Li^+ ions is restricted in narrow potential wells over a very short distance associated with the relaxation polarization process. Therefore, $f_{\max}$ separates the frequency region of long-range mobilities of Li^+ ions from short-range. A long flat tail with onset at low frequency and extending to intermediate

frequency is seen in BZL-25 glass, owing to the presence of a large capacitance associated with the electrodes.

It is found that when the amount of Li_2O increases, the peak frequency ($f_{\max}$) value rises. The values of β at different temperatures, acquired by fitting the experimental data using Eq. (19), have been seen to increase in response to temperature as well as Li_2O content (Fig. 16). For an ideal dielectric material, $\beta = 1$ suggests a single relaxation time (Debye model). But in glasses, β values < 1 indicate a distribution of relaxation times due to local structural variations or defects, rather than ideal, single-time relaxation. A smaller β signifies greater structural heterogeneity and a broader distribution of relaxation times, while β approaching 1 suggests a more homogeneous structure. The increasing trend in β values for a particular glass sample with a rise in temperature implies the loosening of the glass network and consequently weakening of interactions amongst ions and surrounding glass matrices. A similar pattern is exhibited by other investigators for several glass systems [29, 42, 66]. The increase in β values with rising Li_2O content. (β is 0.829 for $x=10$ and 0.928 for $x = 25$ at 663 K) signifies an increase in the structural homogeneity and a smaller distribution of relaxation times. It may be due to increasing $\text{Li}^+ - \text{Li}^+$ interaction with decreasing $\text{Li}^+ - \text{Li}^+$ separation; similar results are reported by Dahiya *et al.* in lithium-containing borate glasses [42]. As shown in Fig. 16, $\beta < 1$ for all glass compositions describes the prevalence of a non-Debye type relaxation process. The change in the stretched exponent ' β ' may be related to the oxygen packing fraction. The stretched exponent ' β ' is a signature of the glass network loosening. As for every one mole of Li_2O that replaces one mole of Bi_2O_3 , two oxygen atoms are lost from the overall composition, thereby reducing the oxygen packing fraction and making the glass network more "open". The stretched exponent ' β ' obtained from the experimental data (Fig. 16) is found to increase with an increase in the Li_2O content (decrease in oxygen packing fraction) and temperature.

The stretched exponent β is found to be temperature and composition-dependent in the studied glass system, while β is temperature independent in Li-free glasses [60].

To comprehend the relaxation mechanism, its temperature as well as composition dependence, experimentally obtained data of the electric modulus' imaginary component, M'' , is scaled using $M''_{\max}$ and $f_{\max}$ as the scaling parameters. A typical scaling plot for BZL-25 glass is shown in Fig. 17. It is clearly visible from the figure that temperature-dependent scaling spectra are superimposed into a single master curve in the complete studied temperature range. Other glass samples show similar behavior. The composition-dependent M'' spectra at 653 K and 713 K are present in Figs. 18(a)-(b), respectively, collapse into one master curve within the studied frequency spectral range. Results

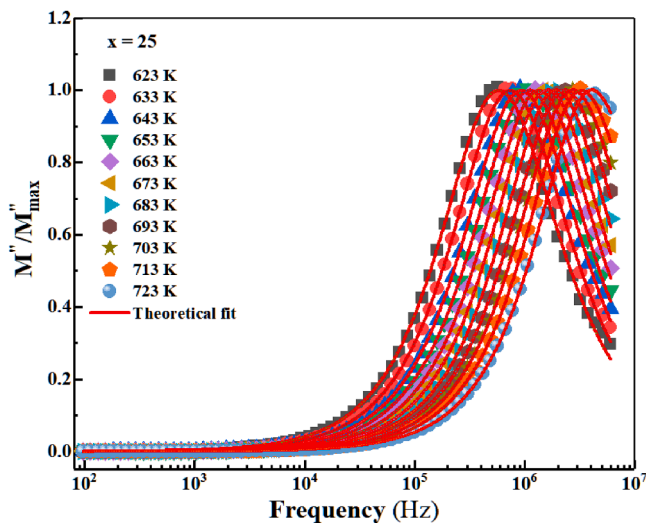


Fig. 15. Fitted electric modulus' imaginary component (M'') vs. frequency spectra at different temp. BZL-25 glass using Eq (19).

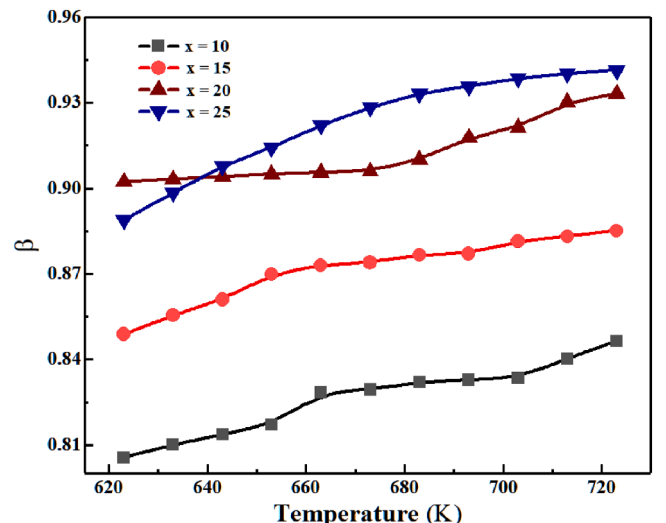


Fig. 16. Temperature dependency of frequency exponent (β) for BZL glasses.

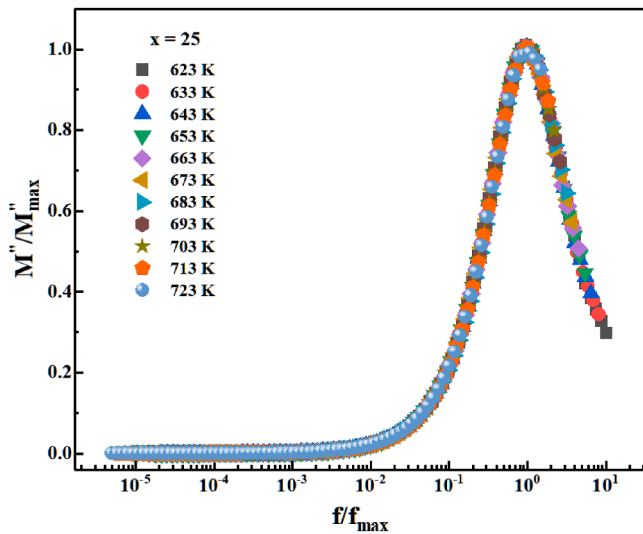


Fig. 17. Scaled frequency dependent spectra of electric modulus' imaginary component (M'') at distinct temperatures for BZL-25 glass.

obtained from modulus formulation closely like those found from the impedance analysis and confirm the existence of the identical kind of relaxation mechanism in every glass specimen.

The relaxation frequency (f_{max}) acquired by fitting the experimental values of M'' vs. frequency at distinct temperature values for all glasses using Eq. (18) has been utilised to find the relaxation time ($\tau_{M''}$) using the relation as [42]

$$\tau_{M''} = \frac{1}{2\pi f_{max}} \quad (19)$$

The calculated values of relaxation time ($\tau_{M''}$) using Eq. (19) for the presently studied set of glasses are found to lie in the range 0.039 μ s to 1.48 ms. As presented in Fig. 19, $\tau_{M''}$ exhibits an alleviating tendency with upsurge in Li_2O amount in understudy set of glass specimens, this is an obvious pattern as the conductivity of the studied glasses escalates with rising Li_2O concentration. The relaxation time ($\tau_{M''}$) follows Arrhenius behavior, and hence, the associated activation energy (E_R) is determined from slopes of $\tau_{M''}$ vs $1000/T$ graph as

$$\tau_{M''} = \tau_0 \exp\left(\frac{E_R}{k_B T}\right) \quad (21)$$

where τ_0 denotes the pre-exponential factor, k_B and T represent the Boltzmann constant and absolute temperature value. The linearly fitted plots of $\log \tau_{M''}$ and $1000/T$ (goodness of fitting parameter (R^2) in the range 0.989 - 0.998) for the set of glass specimens are portrayed in Fig. 19, and acquired activation energy (E_R) values are listed in Table 4. E_R shows a decreasing trend with the addition of Li_2O amount.

4. Conclusions

Investigations on dielectric properties of the presently studied glasses were done in the frequency spectrum 100 Hz to 5 MHz and temperature range 623 K to 723 K with varying Li_2O concentration.

Experimentally observed data of ac conductivity is fitted with Jonscher's power law. Quantum Mechanical Electron tunnelling theory of conduction mechanism is found applicable in these glasses. At a given temperature, conductivity increases with Li_2O content. The single depressed semicircular curve in Nyquist plots of understudy glass samples substantiates the presence of a "non-Debye type" single relaxation conduction process. The relaxation time of both electric impedance ($\tau_{Z''}$) and electric modulus ($\tau_{M''}$) exhibit a declining trend with rising Li_2O content. Higher $\tau_{Z''}$ values than corresponding $\tau_{M''}$ values assert long-

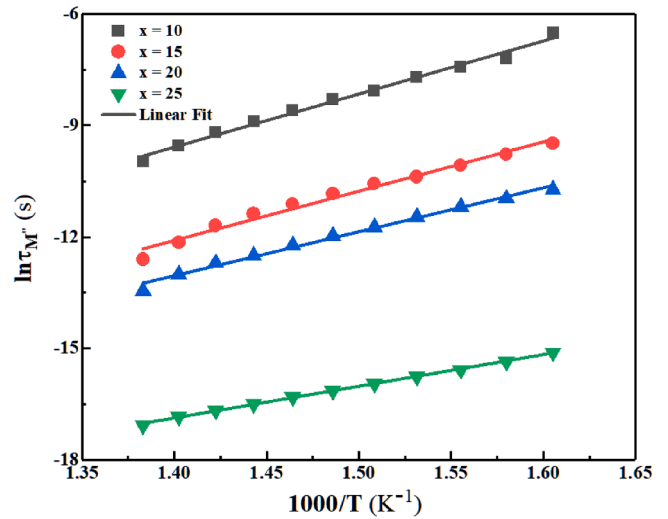


Fig. 19. Linear fits of $\log \tau_{M''}$ vs. $1000/T$ for BZL glass system.

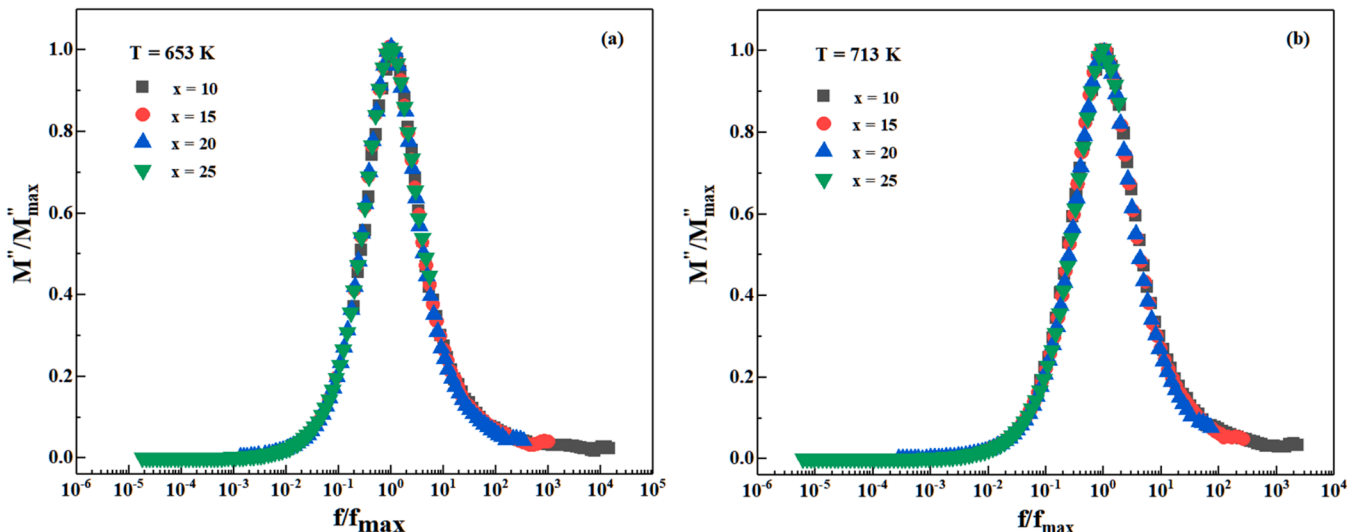


Fig. 18. Scaled imaginary component of electric modulus (M'') at (a) 653 K and (b) 713 K for different BZL glass compositions.

ranged and localized relaxation conductivity. The activation energy of the electric modulus (E_R) declines with the rise in lithium content. However, dc activation energy (E_{dc}) and ac activation energy (E_z) values exhibit a similar trend with increased Li_2O amount. It is observed that, with a rise in Li_2O amount from $x=10$ to $x=15$, the activation energies increase; thereafter, an increase in Li_2O amount causes a decrease in the activation energies. The results of the electric modulus formulation assert the existence of a temperature-dependent relaxation mechanism in the understudy glass specimens. The values of the stretched exponent β are observed to rise as the temperature rises throughout all glass specimens, indicating the decrease in the compactness of the glass network and, hence, weakening the interaction of ions with the surrounding matrix. Scaling spectra of the imaginary component of electric modulus (M'') superimpose into a single master curve for all the temperatures and compositions, thereby confirming the existence of a similar kind of relaxation mechanism in the understudy glass system.

CRedit authorship contribution statement

Manju Bala: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Neha Sehrawat:** Writing – review & editing, Data curation. **Preeti Sharma:** Writing – review & editing, Data curation. **Jaswant K. Yadav:** Writing – review & editing. **Sajjan Dahiya:** Writing – review & editing, Visualization, Validation, Supervision, Software, Methodology, Conceptualization. **R. Punia:** Writing – review & editing, Visualization, Validation, Supervision, Software, Resources, Project administration, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

University Grants Commission (UGC), New Delhi, and the Department of Science and Technology (DST) for providing financial support through the UGC-SAP (F530/5/DRS/2012(SAP-I)) and DST-FIST (SR/FST/PSI-162/2011) grants to the Department of Physics at MDU Rohtak. One of the authors, Neha Sehrawat, acknowledges DST, New Delhi, for the Inspire Fellowship grant as a Senior Research Fellow (IF210233).

Data availability

The data will be made available at request.

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