Solid State Sciences 48 (2015) 230–236

Contents lists available at ScienceDirect

Solid State Sciences

journal homepage: www.elsevier.com/locate/ssscie

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

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A R T I C L E I N F O

*Article history:*
Received 25 June 2015
Received in revised form
19 August 2015
Accepted 20 August 2015
Available online 25 August 2015

*Keywords:*
Jonscher's power law
Overlapping of large polaron tunneling
Polarons
Electric modulus
Relaxation

A B S T R A C T

The ac conductivity of tellurium based quaternary glasses having composition 60 $TeO_2$ − 10 ZnO − (30 − x) $B_2O_3$ − x$Bi_2O_3$; x = 0, 5, 10, 15 and 20 has been investigated in the frequency range $10^{-1}$ Hz to $10^5$ Hz and in the temperature range 483 K–593 K. The frequency and temperature dependent ac conductivity increase with increase in bismuth content and found to obey Jonscher's universal power law. The dc conductivity, crossover frequency and frequency exponent have been estimated from the fitting of the experimental data of conductivity with Jonscher's universal power law. In the studied glasses the ac conduction may be described by overlapping of large polaron tunneling model. The activation energy is found to be decrease with increase in bismuth content and variable range hopping (VRH) proposed by Mott with some modification suggested by Punia et al. is more or less suitable to explain dc conduction. The value of the stretched exponent (β) obtained by fitting of M″ reveals the presence of non-Debye type of relaxation in the presently studied glass samples. Scaling spectra of electric modulus (M′ and M″) collapse into a single master curve for all the compositions and temperatures. The values of activation energy of electric modulus ($E_R$) and conduction (W) are nearly equal for all the studied glasses, indicating that the polaron have to overcome the same energy barrier during conduction as well as relaxation processes. The conduction and relaxation process in the presently studied glass samples are composition and temperature independent.



## 1. Introduction

Heavy metal oxide glasses such as $TeO_2$, $Bi_2O_3$ etc. have been studied extensively in the recent years [1–4] due to their wide applications in the field of glass ceramics, layers for optical and electronic devices, thermal and mechanical sensors, reflecting windows, etc. [5–9]. $TeO_2$ based glasses have low melting temperatures, high dielectric constant, and good infra red transmissions [10–13], which makes them suitable candidates for a wide range of applications such as optical materials used in laser technology [14,15] and fast-ions conducting solid electrolytes [16,17]. Glasses containing $Bi_2O_3$ and ZnO have a long infra red cut off and third order non linear optical susceptibility which make them ideal candidate for application as infra red transmission components and photonic devices [18,19]. Addition of heavy metal oxides (like $Bi_2O_3$, $Nb_2O_3$) to tellurite glasses enhances both the physical and optical properties of these glasses and addition of ZnO to tellurite glass network increases the stability of glass network and glass forming ability [20,21]. The temperature dependence of conductivity of tellurite glasses has been found to show the characteristic transition between conduction in a polaron band and due to hopping [22,23]. The conductivity in these glasses depends on number of mobile charge carriers and their mobility [24]. The electronic transport properties of $TeO_2$ − $Bi_2O_3$, $TeO_2$ − $V_2O_5$ − $Bi_2O_3$, $TeO_2$ − ZnO, $Bi_2O_3$ − $B_2O_3$ − ZnO and other tellurite based glass system have been studied by many researchers [25–30]. But, there is hardly any report in literature on systematically composition and frequency dependent ac conductivity, scaling behavior, electric modulus formulation and conduction mechanism of $TeO_2$ − $Bi_2O_3$ − $B_2O_3$ − ZnO glass system.

In the present study, we report the ac conductivity, dielectric

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http://dx.doi.org/10.1016/j.solidstatesciences.2015.08.016
1293-2558/

properties, electric modulus formulation and relaxation studies of the tellurium based quaternary glasses using impedance spectroscopy.

## 2. Experimental

Glasses having compositions 60 $TeO_2$ − 10ZnO − (30 − x) $B_2O_3$ − x$Bi_2O_3$; x = 0, 5, 10, 15 and 20 were prepared using analar grade ZnO, $Bi_2O_3$, $B_2O_3$ and $TeO_2$ chemicals by melt-quench technique. The detailed discussion of preparation of studied glass system is reported elsewhere [1]. X-ray diffraction studies of the samples performed using Rigaku Table-Top X-Ray Diffractometer confirm the amorphous nature of these samples. The values of glass transition temperature ($T_g$) of different samples were measured by DSC technique using T A Instruments, Model no. Q600 SDT, at a heating rate 10 °C/min in nitrogen atmosphere. The glass samples were cut and ground to get rectangular shapes with thickness about 1 mm and their surfaces were polished. For electrical measurements, both sides of the polished samples were coated with silver to serve as electrodes. Conductivity measurements were carried out by using Alpha-A high resolution dielectric, conductivity, impedance, and gain phase modular measurement system by Novocontrol Technologies GmbH & Co. KG in the frequency range of $10^{-1}$ Hz to $10^5$ Hz and temperature ranging from 483 K to 593 K. The fitting of experimental data was done by using linear fit and non-linear curve fitting modules of Origin Pro 8.6 software.

## 3. Results and discussion

The ac conductivity of different glass compositions of 60 $TeO_2$ − 10ZnO − (30 − x) $B_2O_3$ − x$Bi_2O_3$; x = 0, 5, 10, 15 and 20 glass system recorded in temperature range 483 K–593 K and frequency range $10^{-1}$ Hz to $10^5$ Hz show similar frequency and temperature dependence. The frequency dependent conductivity goes on increasing with increase $Bi_2O_3$ content in studied frequency range at any particular temperature, a typical compositional variation of σ′(ω) with frequency at 553 K is shown in Fig. 1.

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

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

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

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

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

(i) If s decreases with temperature then it follows correlated barrier hopping (CBH) conduction mechanism [40].
(ii) If s depends upon frequency but is in dependent of temperature then the conduction mechanism can be explained by the quantum mechanical electron tunneling theory [40].
(iii) If s increases with increase in temperature, then the conduction process can be explained with the small polaron quantum mechanical tunneling theory where as if s decreases at first, reaching a minimum and increases thereafter with increase temperature then it can be explained by large polaron quantum mechanical tunneling model [40].

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

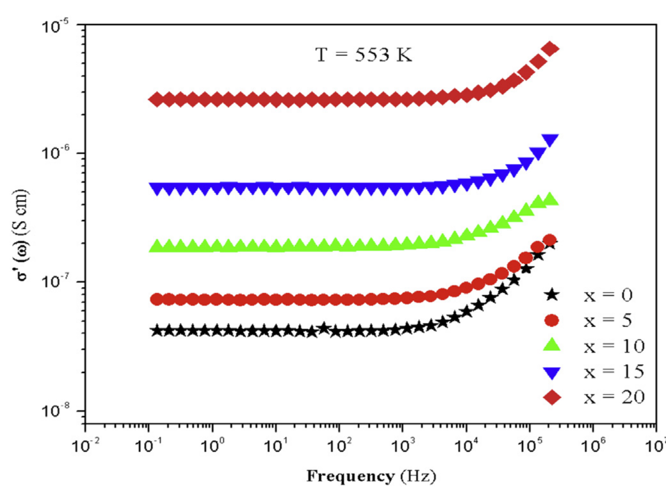


**Fig. 1.** Compositional variation of total ac conductivity σ′(ω) of 60 $TeO_2$ − 10ZnO − (30 − x) $B_2O_3$ − x$Bi_2O_3$ glass system at 553 K.

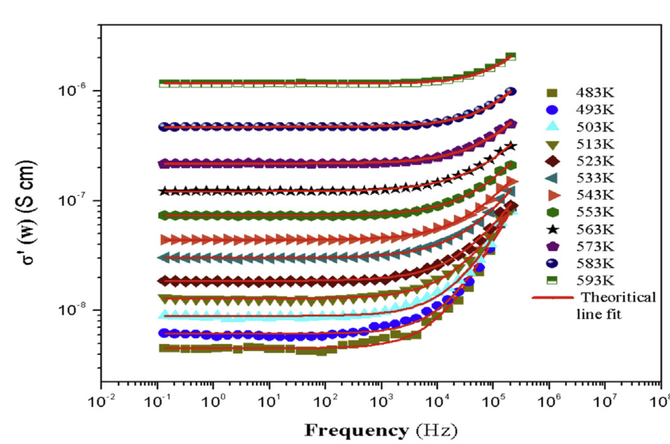


**Fig. 2.** Measured total ac conductivity (σ′) for 60 $TeO_2$ − 10ZnO − (30 − x) $B_2O_3$ − x$Bi_2O_3$ glass composition shown as function at twelve different temperatures. The solid lines in the figure are the best fits obtained from fitting of experimental data with Jonscher's power law.