

RESEARCH ARTICLE

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Study of Dielectric Relaxation in $60\text{B}_2\text{O}_3 - 10\text{TeO}_2 - 5\text{TiO}_2 - 25\text{R}_2\text{O}$ (R= Li, Na & K) Quaternary Glass System.

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Abstract

Glasses with composition $60\text{B}_2\text{O}_3 - 10\text{TeO}_2 - 5\text{TiO}_2 - 25\text{R}_2\text{O}$ (R= Li, Na & K) have been prepared using normal melt-quench technique. Dielectric measurements were carried out in the frequency range from 100Hz to 1MHz and in temperature range from room temperature (RT) to 350°C by using alternating current impedance spectroscopy. The dielectric constant values increase with increase in temperature. Dielectric value lies in the range of 30-170 for lithium, 30-80 for sodium and 32-60 for potassium containing boro tellurite glasses. It is also found that dielectric constant values decrease with increasing frequency. The temperature dependence of the dielectric constant $\epsilon'(\omega)$ shows that, at relatively lower temperature, the electric dipoles formed in the glasses are frozen and rotated at the softening temperature of the glass.. At elevated temperature the glassy network gets relaxed while, motion charge carrier and dipoles become easier. Each $\epsilon'(\omega)$ and $\epsilon''(\omega)$ was found to be dependent on the alkali oxide. Dielectric constant values are found to be high for lithium containing glass

Keywords: Dielectric relaxation, Transport properties, Impedance spectroscopy, Dielectric constant, Tellurite glasses

I. Introduction

Boro-tellurite glasses have been widely studied in literature because of the industrial importance of tellurite in making glasses with desirable optical properties. Since both B_2O_3 and TeO_2 are present in boro tellurite glasses, it leads to complex specification and interesting glass structure. Introduction of alkali ions in these glasses exhibit high electrical conductivity and hence can also be a potential candidate for application in solid state - electrochemical devices such as batteries, sensors, etc. [1]. Among various types of glasses, the tellurite glasses exhibit high dielectric constant and electrical conductivity, which has been argued to be due to the unshared pair of electrons of the TeO_4 group that do not take part in the bonding [2].

In addition, Tellurium dioxide based glass have peculiar characteristics such as good infrared transmission, low melting temperature and high third order non-linear susceptibility. Tellurium dioxide also exhibit two types of structural units, $\text{TeO}_4(\text{tbp})$ and $\text{TeO}_3(\text{tp})$ which makes this glass in technological importance. Work has been done on dielectric properties of tellurium based glasses for $\text{TeO}_2 - \text{P}_2\text{O}_5$ glasses by M.M Elkholy et al [3], Lithium ion conductivity has been investigated in boro-tellurite glass system [4]. Glass formation region, electrical conductivity and structure of $\text{AgI-Ag}_2\text{O-B}_2\text{O}_3\text{-TeO}_2$ glasses have been investigated in detail [5].

Dielectric properties of $\text{ZnF}_2\text{-PbO-TeO}_2$ glasses have been studied [6]. Recently, authors

studied on $60\text{B}_2\text{O}_3 + 10\text{TeO}_2 + 5\text{TiO}_2 + 24\text{R}_2\text{O} : 1\text{CuO}$ (where R=Li, Na, K) glass system by ESR, IR, Raman and optical absorption studies [7], AC conductivity and impedance measurements [1] and studies on cadmium boro tellurite glasses [8].

Present work is mainly aimed to study the frequency and temperature dependencies on the dielectric constant for $60\text{B}_2\text{O}_3 - 10\text{TeO}_2 - 5\text{TiO}_2 - 25\text{R}_2\text{O}$ (where R=Li, Na & K) quaternary glass system

II. Experimental

For experimental studies, a quaternary $60\text{B}_2\text{O}_3 - 10\text{TeO}_2 - 5\text{TiO}_2 - 25\text{R}_2\text{O}$ glass system was prepared by conventional melt quenching method. For each glass, all preparation conditions were similar. All glass samples prepared in a disc form. Glassy nature of the samples was confirmed by XRD studies. Compositions of the glasses are studied and their corresponding codes are listed in Table.1. Dielectric measurements were carried out using Frequency Resonance Analyzer (FRA) (Auto Lab, PGSTAT 30) for different frequencies in the range of 100 Hz to 1 MHz and temperature from room temperature (RT) to 350°C . The real and imaginary parts of the complex impedance terms of all glass samples were measured as the function of temperature and frequency.

Table.1 Compositions of the Series BTTR
(where R=Li, Na &K)

Sl.No	Code	Composition (mol %)
01	BTTL	60B ₂ O ₃ -10TeO ₂ -5TiO ₂ -25Li ₂ O
02	BTTN	60B ₂ O ₃ -10TeO ₂ -5TiO ₂ -25Na ₂ O
03	BTTK	60B ₂ O ₃ -10TeO ₂ -5TiO ₂ -25K ₂ O

III. Results & Discussion

The frequency dependence of real and imaginary part of dielectric permittivity $\epsilon'(\omega)$ and $\epsilon''(\omega)$ respectively at various temperatures for all the glass samples are shown in Fig.1a ,b & c & 2a, b & c. The $\epsilon'(\omega)$ and $\epsilon''(\omega)$ gradually increases as the temperature increases. All the other glasses in the present study show similar behavior. From the figure, it is clear that at a particular temperature the value of $\epsilon'(\omega)$ decreases with increasing frequency and attains a lower value which is not related to the hopping dynamics of mobile ions. This is associated with electrode polarization arising usually from space charge accumulation at the glass-electrode interface. The lower value at high frequency, results from the rapid polarization processes occurring in the glass sample. Furthermore, The high values of $\epsilon'(\omega)$ are obtained in low frequency region arising due to the presence of metallic or blocking electrodes which do not permit the mobile ions to transfer into external circuit, as a result mobile ions pile up near the electrodes and give a large bulk polarization in the materials [9].

Fig.3 shows $\epsilon'(\omega)$ and $\epsilon''(\omega)$ as a function of frequency at particular temperature 300°C. It shows that dielectric constant values are high for lithium followed by sodium and potassium but this amount of increase between sodium and potassium is negotiable. This may be due to fact that lithium ions hop easily out of the sites with low free energy barriers in the field direction and tend to accumulate at sites with high free energy barriers in the lower frequency region. This leads to a net polarization of the ionic medium and gives higher dielectric constant values [10], however, at higher frequency, the charge carriers will no longer be able to rotate rapidly, so their oscillation will begin to lay behind this field, resulting in a decrease of dielectric constant.

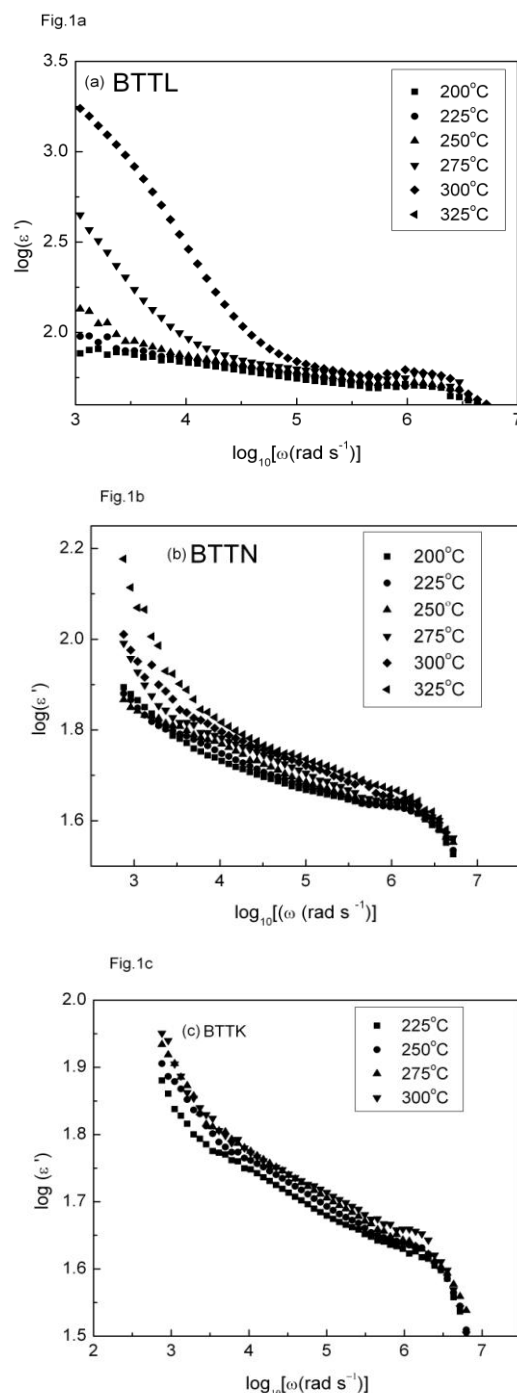


Fig.1 Frequency dependence of $\epsilon'(\omega)$ for
a) BTTL, b) BTTN & c) BTTK glasses

The observed alkali oxide dependence of dielectric constant is similar to that of ac conductivity (8), authors have explained ac conductivity and impedance measurements on the

present glass system where it is found that ac conductivity is more for lithium followed by potassium and sodium but this amount of increase between sodium and potassium is negotiable, because glass network create an easy paths for the movement of lithium ions, which in turn increase ac conductivity as compared to sodium and potassium, when replaced for lithium.

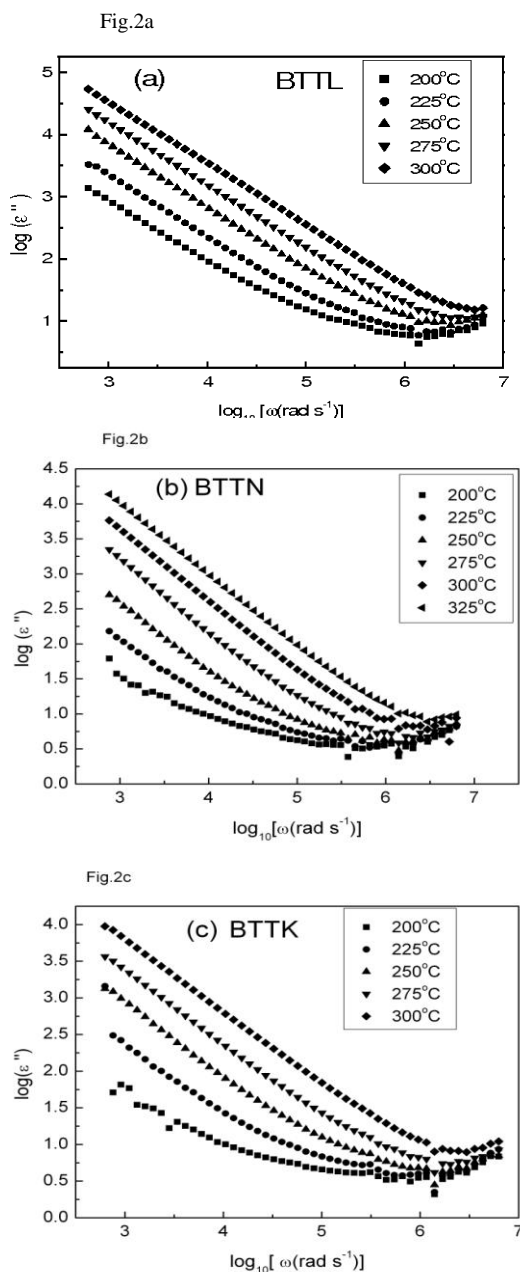


Fig.2. Frequency dependence of $\epsilon'(\omega)$ and $\epsilon''(\omega)$ for a)BTTL, b) BTTN & c) BTKK glasses

Alkali dependence in the present study can be explained as, when one type of alkali ion is replaced by one another, glass network is weakened

and creates pathways ($\text{Li} > \text{Na} > \text{K}$) suitable for alkali ion migration, causing space charge build up and increase in dielectric parameters, $\epsilon'(\omega)$, $\epsilon''(\omega)$ and $\tan\delta$. The temperature dependence of $\epsilon'(\omega)$ at different frequencies for all investigated glasses are given in Fig 4a,b & c. At lower temperatures, $\epsilon'(\omega)$ value increases slightly with increase in temperature for all prepared glasses. In addition, a large variation of $\epsilon'(\omega)$ is observed at a relatively higher range of temperature (in the region where the glass started to be soft). The rate of increasing $\epsilon'(\omega)$ with temperature was found to decrease with increasing frequency (Fig.4). The observed behaviour of temperature dependence of $\epsilon'(\omega)$ in our glass system is consistent with the results of M. G. El - Sharawy & F. H. El Batal [11]

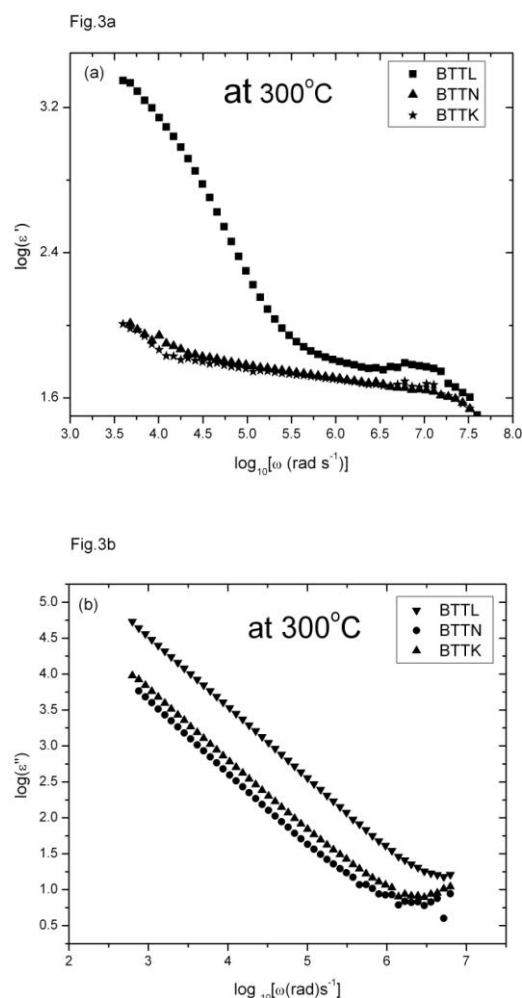


Fig.3. Frequency dependence of $\epsilon'(\omega)$ and $\epsilon''(\omega)$ for BTTL, BTTN & BTKK glasses at 300°C

where, increase in temperature facilitated the dipolar orientation in the glasses resulting in increase in $\epsilon'(\omega)$. Dielectric constant values are found to lie in the range 30-170 for BTTL glass, 30-80 for BTTN

and 32-60 for BTTK. Likewise dielectric constant values of our study show similarity to the values of M. M. Ahmad et.al [12] and values of A. Mogus et al [13]. The increase of ϵ' with increase in temperature is usually associated with the decrease in bond energies[14]

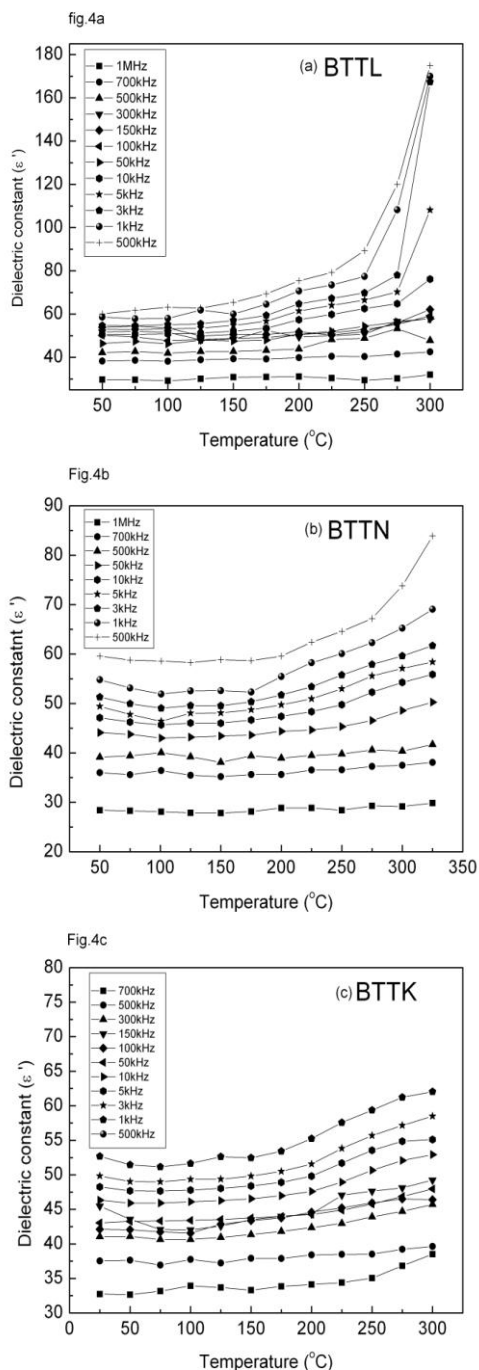


Fig.4. Temperature dependence of dielectric constant for BTTL, BTTN & BTTK glasses

That is, as the temperature increases two effects on the dipolar polarization may occur: (1) it weakens the intermolecular forces and hence enhances the orientational vibration, (ii) it increases the thermal agitation and hence strongly disturbs the orientational vibrations. The dielectric constant becomes larger at lower frequencies and at higher temperatures which is normal in oxide glasses and is not an indication for spontaneous polarization [14]. This may be due to the fact that as the frequency increases, the polarizability contribution from ionic and orientation sources decreases and finally disappears due to the inertia of the ions.

In the present study the glass system can be assumed to exist in the form of molecular dipoles which remain frozen at low temperature and as the temperature is increased, the dipoles attain freedom of rotation even though the material remain in the solid state. Furthermore, at elevated temperature the glassy network is going to relax and the motion of charge carrier and dipoles become easier. Thus $\epsilon'(\omega)$ should increase with temperature. This increase can also be attributed to raising the charge concentration (due to dangling bonds), which enhances the electron relaxation polarization. The observed behaviour of $\epsilon'(\omega)$ can also be understood according to that the dipoles exist corresponding to polaron hopping between sites of different energies or polaron hopping about structural defects. If polaron hopping occurs between sites with a certain statistical rate, the polarization will have a very small lag with the applied field for frequencies much more lower than the hopping rate but the magnitude of polarization will decrease with increasing frequencies. By increasing the frequencies, the orientable dipoles will no longer be able to rotate rapidly enough and hence the cooperation to the polarization as well as the dielectric constant $\epsilon'(\omega)$ decrease. The dispersion occurring during transition from high orientable polarization at frequency to negligible orientable polarization at high frequency is seen as a decrease in $\epsilon'(\omega)$ values with increasing frequency.

IV. Conclusions

The frequency dependent dielectric constant in some alkali boro tellurite glasses are studied over a frequency range from 100 Hz to 1MHz and in a temperature range from room temperature to 350°C by alternating current impedance spectroscopy. Each $\epsilon'(\omega)$ and $\epsilon''(\omega)$ were found to depend on the alkali oxide. When one type of alkali oxide is replaced by one another, glass network is weakened and creates pathways (Li > Na > K) suitable for alkali ion migration, causing space charge build up and increase in dielectric parameters, $\epsilon'(\omega)$, $\epsilon''(\omega)$ and $\tan\delta$, which are found to high for lithium followed by sodium and potassium containing boro tellurite

glasses. Dielectric values lies in the range 30-170 for lithium, 30-80 for sodium and 32-60 for potassium containing boro tellurite glasses. Decrease in dielectric constant with increase in frequency is attributed to the decrease in electronic contribution and increase in dipolar contribution to the total polarizability with increase of frequency.

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