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DIELECTRIC, AC CONDUCTIVITY AND OPTICAL PROPERTIES OF MIXED IONIC-ELECTRONIC $20Li_2O$-xBi_2O_3-$(80-x)TeO_2$ TELLURITE GLASS

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ABSTRACT

Mixed ionic electronic $20Li_2O$-xBi_2O_3-$(80-x)TeO_2$; (x = 3-15 mol%) glasses have been prepared by melt-quenching method to investigate the effect of bismuth on dielectric and ac conductivity behaviors. Structural properties of the glasses was investigated by Fourier Transform Infrared (FTIR) spectroscopy. Dielectric properties, ac conductivity and modulus formalism of the glasses were investigated by using impedance spectroscopy measurements in the frequency range of 0.01Hz to 1MHz and in the temperature range of 323 K - 473 K. IR spectra of the present glass system shows Bi_2O_3 plays the role of network former with BiO_3 unit structure at $x \leq$ 7 mol% but acts as network modifier with BiO_6 unit structure for $x \geq 10$ mol%. Transference number measurements showed the glasses were initially predominantly ionic for $x \leq 7$ mol% before a large drop in ionic contribution accompanied by increase in electronic carrier for $x \geq 10$ mol% where the glasses transform into mixed ionic electronic glass with ionic conduction still as the major component. The dielectric constant ε' and ac conductivity showed increasing trend with the increase in Bi_2O_3 except for an unexpected drop at $x = 7$ mol%. The anomalous drop is suggested to be due to mixed ionic electronic (MIE) effect which involves some form of hindering effect of Bi_2O_3 on Li^+ ions. The drop in ionic conductivity in the $x \geq 10$ mol% region is suggested to be due to some form of hindering effect of the heavier Bi^{3+} on Li^+. AC conductivity showed weaker dispersion at low frequency ($f <$ 100Hz) and exhibited stronger dispersion at higher frequency ($f >$ 100Hz) where in the dispersion region, the charge transport mechanism was found to be Correlated Barrier Hopping (CBH) for all glass samples except for x = 7 mol% where the charge transport mechanism was Overlapping Large Polaron Tunneling (OLPT) at low frequency ($f <$ 100Hz) and CBH mechanism at high frequency ($f >$ 100Hz) respectively. The imaginary part of electrical modulus spectra was fitted to the Kohlrausch-Williams-Watts (KWW) stretched exponential function and the value of the stretched exponent, β which represents the degree of interaction between the ions was found to be dependent on composition. Bi_2O_3 addition to $20Li_2O$-xBi_2O_3-$(80-x)TeO_2$ glasses resulted in slow decrease of optical band gap E_{opt} up to x = 13 mol% before a large drop at higher Bi_2O_3 content (x = 15 mol%). This optical behaviour is suggested to be related to changes in non bridging oxygen NBO content in the glass system in conjunction to presence of defects in the glasses. Urbach energy E_u shows opposite behaviour with E_{opt} indicating electron transition from the top of valence band to lowest defect state. On the other hand, the variation of refractive index n is influenced by electronic polarizability α_o^{2-}. Addition of bismuth at $x \geq 7$ mol% showed n increased due to increase in α_o^{2-} as a result of increase in NBOs as NBOs bind electron less tightly than BOs and makes NBO more polarizable.

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CHAPTER ONE
INTRODUCTION

1.1 BACKGROUND OF STUDY

Tellurium oxide (TeO_2) glasses have attracted great interest on account of their good properties such as thermal stability, high dielectric constants, high refractive indices and low glass transition temperature compared to other glass systems (Rajendran, Palanivelu, Chaudhuri, & Goswami, 2003; Udovic et al. 2006; M.Rada, Rus, S.Rada, Culea, & Rusu, 2014; Rani, Sanghi, Ahlawat, & Agarwal, 2014). Tellurite glass is formally known as a conditional glass former hence pure TeO_2 is not stable and crystallizes easily (Fares, Jlassi, Elhouichet, & Férid, 2014). Due to the reason, tellurite is not able to form glass without the aid of modifier such as alkali metal oxide, alkaline earth metal oxide, transition metal oxide or other glass modifiers (Yahia et al. 2009; Azianty, Yahya, & Halimah, 2012). Tellurite based glasses changes its basic structural unit from TeO_4 trigonal bipyramid (tbp) (Sokolov, Plotnichenko, Koltashev, & Grishin, 2009; Kaur & Khanna, 2014) to TeO_3 trigonal pyramid (tp) (Ali & Shaaban, 2008; Gaafar, Abdeen, Mostafa, & Marzouk 2011; Yousef, Sayed, Al-Qaisi, & Badriah 2013) when doped with glass modifiers.

Addition of alkali metal oxides into tellurite glass induced the glass to exhibit ionic conductivity such as reported in $x$$Na_2O$-(1-$x$)$TeO_2$ and 0.4Li_2O-0.6[$x$$P_2O_5$-(1-$x$)$Te_2O_4$] glass (Jayasinghe, Coppo, Bandaranayake, & Souquet, 1995; Jayasinghe, Bandaranayake, Dissanayake, & Gunawardane, 1995). On the other hand, tellurite glasses containing transition metal oxides such as V_2O_5, Fe_2O_3, WO_3 and MoO_3 shows electronic conductivity behaviour which is attributed by polaron conduction mechanism. Several studies have suggested that in binary V_2O_5-TeO_2 glasses, electronic conductivity takes place due to the multivalency of vanadium ion (Laila, Supardan, & Yahya, 2013). The polaron conduction mechanism arise from the hopping of electron from V^{4+} site to V^{5+} site of V_2O_5 which induces polarization of the lattice and forms polaron (Srilatha et al. 2011; Mirzayi & Hekmatshoar, 2013). Interestingly, glasses can also have mixed ionic-electronic conductivity with presence of both monovalent cations and transition metal oxides. Several mixed electronic-