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Structural, Dielectric and AC Conductivity Behavior of Multicomponent TeO_2-ZnO-Li_2O-Na_2O-B_2O_3 Glasses

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Multicomponent glasses of the TeO_2-ZnO-Li_2O-Na_2O-B_2O_3 (TZLNB) system have been prepared by conventional melt quenching method. Synthesized glasses were characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR), Raman and UV-Visible spectroscopic techniques. The amorphous nature of these glasses has been confirmed by their XRD pattern. In the present TZLNB glass, B_2O_3 is found to transform into a complex network, which involves a boroxol ring coupled with a fourfold-coordinated boron (BO_4) due to non-bridging oxygens. The frequency dependences of dielectric constant (ε'), dielectric loss tangent ($\tan\delta$) and ac conductivity (σ_{ac}) studies have been undertaken on the TZLNB glasses in the frequency range 50 Hz-5 MHz at room temperature. Dielectric properties such as dielectric constant and dielectric loss tangent are found to decrease with increasing frequency. Present TZLNB glasses are found to possess high dielectric constant and very low dielectric loss in the studied frequency range. Further, ac conductivity is found to increase with increasing frequency due to an increased density of mobile ions for conduction. Present TZLNB glasses possess excellent dielectric properties such as high dielectric constant and very low dielectric loss and thought to be the most promising dielectric material for the memory cell capacitors in dynamic random-access memory (DRAM) chips.

Keywords: Oxide glasses, FTIR, Raman, Dielectric constant, Dielectric loss tangent, Conductivity analysis.

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1. INTRODUCTION

Glasses having high transparency, high chemical durability and excellent thermal, optical and electrical properties are an important class of materials in microelectronics, optics and optical fiber technology. Since the past several years, borate glasses have attracted much attention due to their electrochemical and optical applications, namely as solid-state batteries, optical waveguides and luminescent materials. It has been observed that certain borate glasses are of much interest and relevance because of their suitability in the progress of waveguide, magneto-optic materials, solid-state laser materials and optoelectronic devices [1-4]. Recently, increasing demand for high-density memories has necessitated the search for new materials with high dielectric constants to fulfill the charge storage density requirements. There has been growing interest in the use of materials with high dielectric constant for capacitors in dynamic random-access memory (DRAM) chips. Particularly, borate glasses with alkali ions are considered as an important class of materials in microelectronics, optics and optical fibers due to their scientific and technological aspect [3].

The doping of TZLNB glasses with other network formers, such as tellurium dioxide (TeO_2), can offer additional modification of their physical properties. Tellurite containing glasses have recently gained wide attention because of their potential as hosts of rare earth elements for the development of fibers and lasers covering all the main telecommunication bands and promising materials for optical switching devices [5, 6]. Further, tellurite containing glasses also exhibit a range of unique properties for potential applications as pressure sensors or new laser hosts [7]. The addition of TeO_2 into borophosphate glasses was found to induce useful properties, including low melting temperature, high refractive indices, high transmission in the infrared region, high dielectric constant, etc., which can find wide application in fiber optics and laser technology [8, 9].

In the present work, TeO_2-doped mixed alkali zinc borate glass (TeO_2-ZnO-Li_2O-Na_2O-B_2O_3) has been synthesized by melt quenching method. Structural, dielectric and ac conductivity studies have been undertaken on the synthesized glass sample.

2. EXPERIMENTAL

Multicomponent TeO_2-ZnO-Li_2O-Na_2O-B_2O_3 glass system having the chemical composition $0.1TeO_2$ + 19.9ZnO + $25Li_2CO_3$ + $5Na_2CO_3$ + $50B_2O_3$ was prepared by using analar-grade chemicals of TeO_2, ZnO, Li_2CO_3, Na_2CO_3 and B_2O_3 as starting materials with 99.9 % purity. These mixtures are sintered at 500 °C and melted in the furnace in a porcelain crucible around 950 °C for 2 h. The melt is then quenched at room temperature between two smooth surface brass plates to form glass. The amorphous nature of the as-quenched sample is confirmed by XRD. The FTIR spectra (400-4000 cm^{-1}) of the as-prepared sample were recorded on a Bruker Alpha spectrophotometer in KBr pellets. The Raman spectrum was recorded on a FT Raman spectrophotometer (Model: Thermo-Nicolet 6700). The optical absorption spectra of polished glass samples were recorded on an UV-VIS-NIR spectrophotometer (Model: Ocean Optics, USB 4000, USA) in the range of 200-900 nm. Dielectric studies on the TZLNB glass system have been undertaken using an impedance analyzer

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model HIOKI 3532-50 LCR HiTESTER Version 2.3. The measurements were carried out at room temperature in the frequency range 50 Hz-5 MHz. The capacitance value (C), dielectric loss tangent ($\tan\delta$) and ac conductance (G) were directly obtained from the instrument. The dielectric constant (ε') and ac conductivity (σ) were calculated using the following relations:

$$\epsilon' = \frac{Cd}{\epsilon_0 A}, \quad (1)$$

$$\sigma_{ac} = \frac{Gd}{A}, \quad (2)$$

where C is the capacitance, d is the thickness of the sample, A is the cross-section area and ε_0 is the permittivity of free space.

3. RESULTS AND DISCUSSION

Fig. 1 displays the XRD pattern of a TZLNB glass sample. The absence of sharp peaks in the present XRD pattern indicates the amorphous nature of the prepared glass sample.

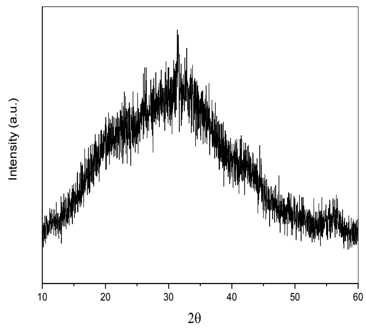

Fig. 1 – XRD pattern of the TZLNB glass sample

The FTIR spectrum of the TZLNB glass sample is shown in Fig. 2. The vibrational modes of the borate network are seen to be primarily active in three infrared spectral regions: (i) the first group of bands which occur at around 1200-1600 cm $^{-1}$ is due to asymmetric stretching relaxation of the B–O band of trigonal BO_3 units, (ii) the second group lies between 800 and 1200 cm $^{-1}$ and is due to B–O bond stretching of tetrahedral BO_4 units, and (iii) the third group is observed around 724 cm $^{-1}$ and is due to bending of B–O–B linkages in the borate networks. The band at 2871 cm $^{-1}$ can be attributed to hydrogen bonds, and a broad band at 3372 cm $^{-1}$ is due to the hydroxyl group (due to stretching of OH^-) [10]. The low-frequency bands in the FTIR spectra of investigated glasses can be attributed to vibration of metal cations present in the glass [10]. A strong absorption peak around 454 cm $^{-1}$ is assigned to the characteristic vibration of lithium cation [11]. Absorption bands in the region 400-550 cm $^{-1}$ are due to ZnO tetrahedron in glasses [12]. The bands around 560 cm $^{-1}$ are assigned to specific vibrations of Co–O bonds [13]. Further, absorption bands around 620-680 and 720-780 cm $^{-1}$ correspond to the Te–O bonds in TeO_4 structural units and Te–O bonds in TeO_3 structural units, respectively [14].

The Raman spectrum of TeO_2-ZnO-Li_2O-Na_2O-B_2O_3 glass is shown in Fig. 3. It exhibits bands at around 250, 318, 458, 553, 685, 775, 780, 947, 1062, 1145, 1353 and 1438 cm $^{-1}$. In the literature, it has been reported that pure B_2O_3 exhibits a strong band at 806 cm $^{-1}$, which was assigned to boroxol ring oxygen breathing vibrations involving very little boron motion. However, in the present TZLNB glass, B_2O_3 is found to transform into a complex network which involves a boroxol ring coupled with a fourfold-coordinated boron (BO_4) due to non-bridging oxygens. The peak at 780 cm $^{-1}$ is assigned to breathing vibrations of six member rings with BO_3 triangles replaced by BO_4 tetrahedral units. The band at 553 cm $^{-1}$ is ascribed to a bending mode (B–O–B) of BO_3^{-3} units. The peak at around 947 cm $^{-1}$ is due to a diborate group and the peak at 1062 cm $^{-1}$ is due to vibrations of diborate groups formed from six membered rings that contain two BO_4 tetrahedral units in the structure [1]. The peaks in the higher frequency region are due to BO_2O^- triangles linked to BO_4 units and BO_2O^- triangles linked to other triangular units [1]. The observed peaks at 1145, 1353 and 1438 cm $^{-1}$ are due to the overlap of different modes of vibrations of B–O. Peaks around 458 and 685 cm $^{-1}$ are ascribed to TeO_4 units, and those around 318 and 775 cm $^{-1}$ are attributed to TeO_3 units [15].

Fig. 2 – FTIR spectrum of the TZLNB glass sample

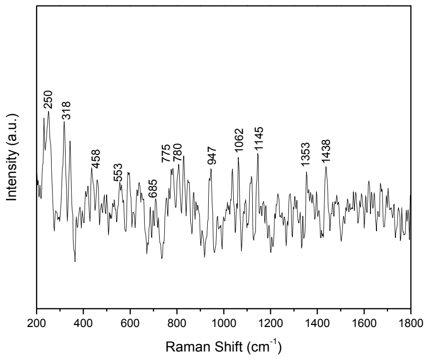

Fig. 3 – Raman spectrum of the TZLNB glass sample

UV-Vis studies have been carried out on the TZLNB glass in the wavelength range 200-900 nm. A typical UV-Vis absorption spectrum of TZLNB glass is shown in Fig. 4. The wavelength corresponding to the maximum absorption for TZLNB glasses is found to be 422.53 nm.

The variation of dielectric constant (ε') with frequency is studied and shown in Fig. 5. From Fig. 5, it is observed that ε' values decrease with increasing frequency. The rate of decrease is found to be lower in the 400 Hz to 500 kHz frequency range. Normally, electronic, dipolar and space charge polarizations are found to contribute to the dielectric constant [16]. With decreasing frequency below 400 Hz, ε' increases due to electrode polarization, arising usually from some space charge accumulation at the glass-electrode interface. In the present studied TZLNB glass system, the measured ε' shows an increase at low frequencies which is attributed to space charge accumulation at the electrode-sample interface. With increasing frequency, the contribution of space charges to the dielectric constant decreases and hence ε' decreases.

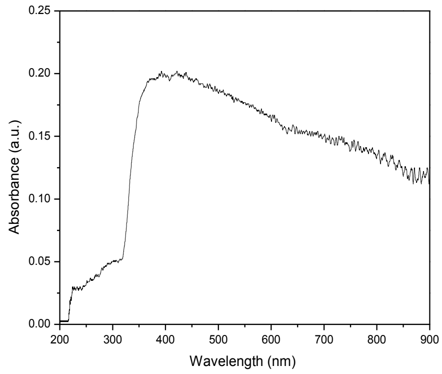

Fig. 4 – UV-Vis absorption spectrum of the TZLNB glass sample

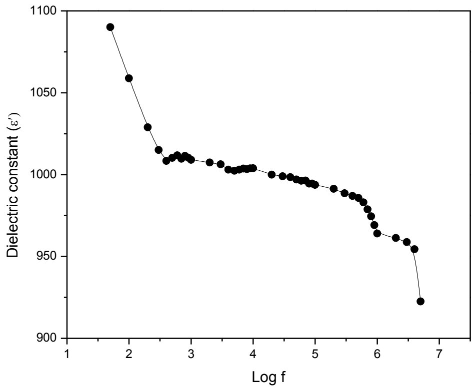

Fig. 5 – Variation of dielectric constant (ε') with frequency

The frequency dependence of dielectric loss tangent (tanδ) at room temperature for TZLNB glasses is shown in Fig. 6. The dielectric loss is found to decrease with increasing frequency. The rate of decrease in dielectric loss is found to be much higher at lower frequencies than at higher frequencies. The present glassy system is found to exhibit lower dielectric loss in the 1 kHz-1 MHz frequency range without much dispersion. The dielectric loss spectra did not show any loss peak in the 50 Hz-5 MHz frequency range, typical of low-loss dielectric materials [17]. It has been observed that low-loss materials show a featureless dielectric response, rather than loss peaks. Similar behavior has also been observed in the ZnO-Na_2O-Al_2O_3-B_2O_3 glass system [17]. Thus, TZLNB glass is a dielectric material with excellent dielectric properties, such as high dielectric constant and very low dielectric loss. It is thought to be the most promising dielectric material for the memory cell capacitors in DRAM chips.

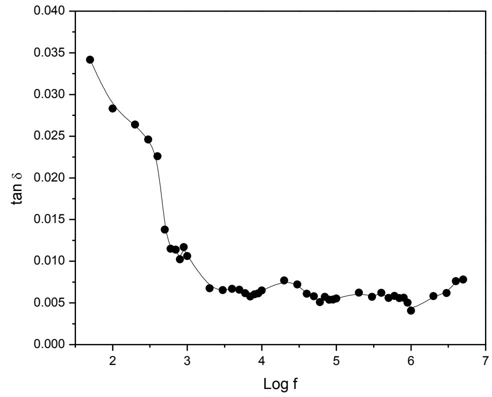

Fig. 6 – Variation of loss tangent (tanδ) with frequency

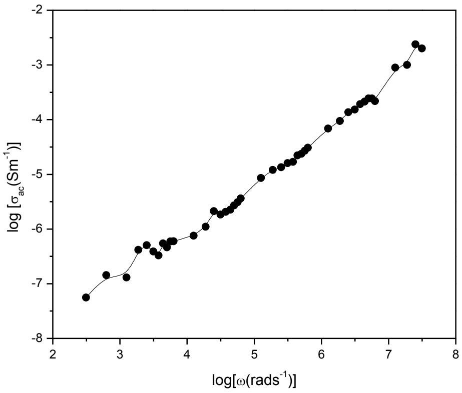

Fig. 7 – Variation of ac conductivity with frequency

Fig. 7 shows the profile of ac conductivity of the TZLNB glass sample, revealing an increasing trend in conductivity with increasing frequency. In the lower frequency region, the enhancement of conductivity with frequency may be ascribed to the interfacial impedance or space-charge polarization [17]. This behavior is well-known in amorphous systems and is attributed to the distribution of relaxation times arising from the disorder.

Fig. 7 displays frequency dependent ac conductivity plots of logσ_{ac} versus logω at room temperature for the TZLNB glass system studied here based on Jonscher universal power law [18]:

$$\sigma(\omega) = \sigma_{dc} + \alpha\omega^s, \quad 0 < s < 1, \qquad (3)$$

where σ_{dc} is the dc conductivity of the sample, a is a constant, $\omega = 2\pi f$ is the angular frequency of the applied field and s is the power law exponent in the range $0 < s < 1$, represents the degree of interaction between mobile ions.

The frequency dependence of conductivity $\sigma(\omega)$ is the sum of dc conductivity due to movements of free charges and ac conductivity (polarization conductivity) due to movements of bound charges. It is observed from logσ_{ac} versus logω plots that the dc plateau disappears due to electrode polarization effects, which are found to cover-up the dc conductivity plateau region in the lower frequency range. Thus, the conductivity curves (dc and ac) tend to merge into a single curve, becoming strongly frequency dependent; these curves show almost a linear behavior (Fig. 7) that follows a power law relation:

$$\sigma(\omega) = a\omega^s, \qquad s < 1. \qquad (4)$$

The value of the exponent is obtained from the slope of log$\sigma_{ac}(\omega)$ versus log(ω) for the curve on the theoretical line fitted by the equation (3). The parameter 's' is linked to the modification of the network structure, and its smaller values indicate a higher degree of modification. The present TZLNB glass sample is found to possess a lower value $s = 0.895$ (< 1), indicating a higher degree of modification of the network structure. Thus, ac conductivity approaches the frequency power law with exponent $s < 1$ and depicts a non-Debye feature [18]. The observed non-Debye type relaxation behavior in the present TZLNB glass may be attributed to the amorphous nature of glasses and distribution of oxide ion sites within glasses to which the ionic jump occurs. A similar behavior was also observed in lithium fluoroborate glasses doped with ZnO and CdO [2] and Co^{2+} doped mixed alkali zinc borate glasses [4].

4. CONCLUSIONS

Novel multicomponent TeO_2-ZnO-Li_2O-Na_2O-B_2O_3 (TZLNB) glass has been prepared by conventional melt quenching method. The synthesized glass was characterized by X-ray diffraction, Fourier transform infrared, Raman and UV-Visible spectroscopic techniques. The amorphous nature of the synthesized glass has been confirmed by its XRD pattern. Dielectric constant (ε') and dielectric loss tangent (tanδ) were found to decrease with increasing frequency. A decrease in the values of ε' and tanδ was attributed to a decrease in the contribution of space charges. The present TZLNB glass was found to possess very low dielectric loss (0.004-0.035) in the studied frequency region. The dielectric loss spectra did not display any loss peak in the 50 Hz-5 MHz frequency range. The ac conductivity of the TZLNB glass sample was found to increase with an increase in the frequency due to an increased density of mobile ions for conduction. Based on the observed trends in the ac conductivity, the present TZLNB glass was found to exhibit a non-Debye behavior. Based on the observed trends in the dielectric constant and dielectric loss tangent, the present glass sample may be employed for DRAM capacitor applications.

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Структурні і діелектричні властивості та поведінка провідності по змінному струму багатокомпонентного скла TeO_2-ZnO-Li_2O-Na_2O-B_2O_3

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Багатокомпонентні стекла системи TeO_2-ZnO-Li_2O-Na_2O-B_2O_3 (TZLNB) були підготовлені звичайним методом загартування розплаву. Синтезовані стекла характеризувались рентгенівською дифракцією (XRD), інфрачервоною спектроскопією з перетворенням Фур'є (FTIR), раманівською спектроскопією та спектроскопією в ультрафіолетовому та видимому діапазонах. Аморфність цих стекол підтверджена їх рентгенограмою. В дослідженому склі TZLNB виявлено, що B_2O_3 перетворюється в складну мережу, яка включає бороксолове кільце, поєднане з чотирикратно скоординованим бором (BO_4) завдяки атомам, які не з'єднуються киснем. Вивчення частотних залежностей діелектричної проникності (ε'), тангенса діелектричних втрат (tanδ) та провідності по змінному струму (σ_{ac}) було проведено на стеклах TZLNB в діапазоні частот 50 Гц-5 МГц при кімнатній температурі. Встановлено, що діелектричні властивості, такі як діелектрична проникність та тангенс діелектричних втрат, зменшуються зі збільшенням частоти. Виявлено, що стекла TZLNB, які розглядаються, мають високу діелектричну проникність і дуже низькі діелектричні втрати в досліджуваному діапазоні частот. Крім того, встановлено, що провідність по змінному струму зростає зі збільшенням частоти через підвищену густину рухомих іонів провідності. Розглянуті стекла TZLNB мають відмінні діелектричні властивості, такі як висока діелектрична проникність і дуже низькі діелектричні втрати, і вважаються найбільш перспективним діелектричним матеріалом для конденсаторів комірок пам'яті в мікросхемах динамічної оперативної пам'яті.

Ключові слова: Оксидне скло, FTIR, Раманівська спектроскопія, Діелектрична проникність, Тангенс діелектричних втрат, Аналіз провідності.