

SYNTHESIS AND DIELECTRIC CHARACTERIZATION OF MnO ADDED ZnO-TeO₂-B₂O₃ GLASSES

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ABSTRACT

Using the conventional melt-quench technique, a glass system of specific composition 20ZnO- (28-x) Te₂O₃-52B₂O₃: x mol% MnO where 'x' varies from 0.5 to 2.0 was synthesized. All the prepared glass samples were examined for their solid-state behavior by XRD and SEM those confirm the non-crystalline state. In this work, three important dielectric properties were experimentally measured across 1 to 100 kHz frequency and room temperature to 200°C range. These parameters show an increasing trend with dopant which confirms the growing degree of disorder due to trivalent manganese ions that acted as modifiers with large concentrations. However, the reasons for variation in activation energy including other dielectric parameters are discussed in detail through the oxidation states of manganese ions and their structural changes.

Keywords: Mn²⁺ ions, tellurite; borate glasses; dielectrics, conductivity.

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INTRODUCTION

Considering the need and demand for glass materials for different electronic device applications, a lot of attention has been paid to the development of novel glasses finding its suitability as hosting materials for lasers, energy storage materials based on high dielectric constant, exhibiting high susceptibility for non-linear optical materials, etc.¹⁻³ Out of several glass-forming oxides borate-based glasses was found to be promising in terms of high chemical stability, moderate melting temperature, simple synthesis, superior optical transparency, dielectric and mechanical properties, the possibility of developing cross-linkages with transition metal oxide ions, etc.⁴⁻⁶ The role of modifier oxide is vital in the borate glass network as it has the significant ability to increase the degree of polymerization in the borate network by converting basic structural trigonal BO₃ units into tetrahedral BO₄ units leading to an increasing structural degree of disorder. TeO₂ is one of the interesting heavy metal oxides that possess high order susceptibilities and its basic structural arrangement in addition to electron occupancy enables them appropriate materials for communication window materials when added with a borate glass system.⁴⁻⁶ Zinc oxide (ZnO) is a fascinating type of modifying oxide known for its ability to generate non-bridging oxygens and induce structural alterations within the fundamental glass framework.⁶⁻⁹ It is intriguing to note that borotellurite glass exhibits a broad tolerance for transition metal oxides, and among them, MnO stands out due to its notable influence on dielectric properties. The various oxidation states of manganese ions, such as divalent and trivalent, further contribute to the modification of dielectric properties in borotellurite glasses by occupying either tetrahedral or octahedral positions. There is a lack of research conducted on the incorporation of MnO in the borotellurite glass system. However, the majority of studies have primarily concentrated on incorporating modifier oxides into borate, phosphate, or silicate glass networks.

Unfortunately, there is a dearth of dielectric investigations specifically concerning MnO-doped borotellurite glass networks. Therefore, an attempt has been made in view of assessing the impact of manganese ions in the borate structure for the dielectric properties. In the present work, the primary objective was to verify the data on glass formation in the ZnO-TeO₂-B₂O₃: MnO composition with subsequent synthesis by melt-quenching technique and to characterize the prepared homogeneous glasses using physical and dielectric characterization techniques.

EXPERIMENTAL

For the preparation of glass samples, a specific composition 20ZnO- (28-x) Te₂O₃-52B₂O₃: x MnO (0 ≤ x ≤ 1.0 mol%) is selected after many attempts. The composition particulars and the corresponding sample notations are summarized below for a better understanding of the results. MnO was added up to 1.0 mol% as samples are losing transparency beyond 1.0 mol%.

MTBT₂: 20ZnO- 27.8 Te₂O₃-52B₂O₃: 0.2 MnO

MTBT₄: 20ZnO- 27.6 Te₂O₃-52B₂O₃: 0.4 MnO

MTBT₆: 20ZnO- 27.4 Te₂O₃-52B₂O₃: 0.6 MnO

MTBT₈: 20ZnO- 27.2 Te₂O₃-52B₂O₃: 0.8 MnO

MTBT₁₀: 20ZnO- 27.0 Te₂O₃-52B₂O₃: 1.0 MnO

The samples were prepared using TeO₂, H₃BO₃, ZnO and MnO, with the weight ratios in mol% considered. Using agate mortar, all the constituent chemical powders were mixed and ground into a smooth powder. The resulting mixture was taken into a platinum crucible and placed in a PID high-temperature melting furnace, where it was heated to 900-950 °C for 30-50 minutes until a transparent molten liquid was obtained. Brass molds were set up to pour the liquid and obtain samples of the desired dimensions. Once the samples were formed, they were transferred to an annealing furnace, which was maintained at a temperature of 350-400°C to prevent any brittleness that might occur. Archimedes' principle has been chosen to determine the density. The experimental density values were then used to calculate the auxiliary material parameters, which helped to investigate the cross-networks and structural changes consisting of glass formers, modifying ions and manganese ions. To test the solid state of the samples, X-ray diffraction was employed. The surface details and size distribution of the grains in the samples were observed through scanning electron microscopic images. Additionally, the dielectric parameters were evaluated using an HP Model 4263-B LCR meter, from 1 KHz to 100 KHz and at temperatures ranging from 30 °C to 200 °C.

RESULTS AND DISCUSSION

The X-ray diffraction patterns confirmed that the glass samples under investigation did not exhibit the typical sharp peaks of crystalline materials. Instead, a broad hump was observed at an angle of diffraction of 2θ = 28°, which can be attributed to the non-crystalline nature. The XRD patterns shown in Fig.-1 remained consistent across all test samples, with no clear evidence indicating a crystalline nature. To characterize the samples for surface morphology, SEM pictures have been taken and confirmed no presence of microstructures or grains. Thus, SEM images evidently support the results of XRD patterns. Consequently, it was determined that none of the prepared glass samples exhibited any form of crystallinity, which can occasionally arise during the conventional annealing process or slow cooling.^{6,8,9} For a better understanding of the morphology of glass samples MTBT₂, MTBT₄, MTBT₆, and MTBT₁₀ are presented in Fig.-2.

Table-1 shows the variation of different parameters with the addition of manganese oxide (MnO) in the borate network. The parameters include average molecular weight, density, concentration of 'Mn' ions, inter-ionic distance, and polaron radius. The substitution of TeO₂ with manganese oxide caused a decrease in the average molecular weight from 96.99 to 96.28 g/mol, which is associated with the fact of MnO molecular weight being lower than that of TeO₂. The reduction in densities from 3.988 to 3.983 g/cm³, although slight, may be related to the fractional addition of manganese oxide. These changes in molecular weight and density indicate a modification in the composition and structure of the borate glass network upon the addition of manganese oxide. As a general observation, the concentration of dopant ions was found to be highest in the sample MTBT₁₀. The range of variation in this concentration was observed from 4.95 x 10²¹ ions to 24.92 x 10²¹ ions per cubic centimeter. Interionic distance r_i (Å) is observed to vary from 0.59

to 0.34 and polaron radius r_p (\AA°) from 0.24 to 0.14 with dopant. The decreasing trend in these parameters confirms that the borate glass network has been incorporated with all the constituent metal ions with a growing degree of changes in the network symmetry.^{10,11}

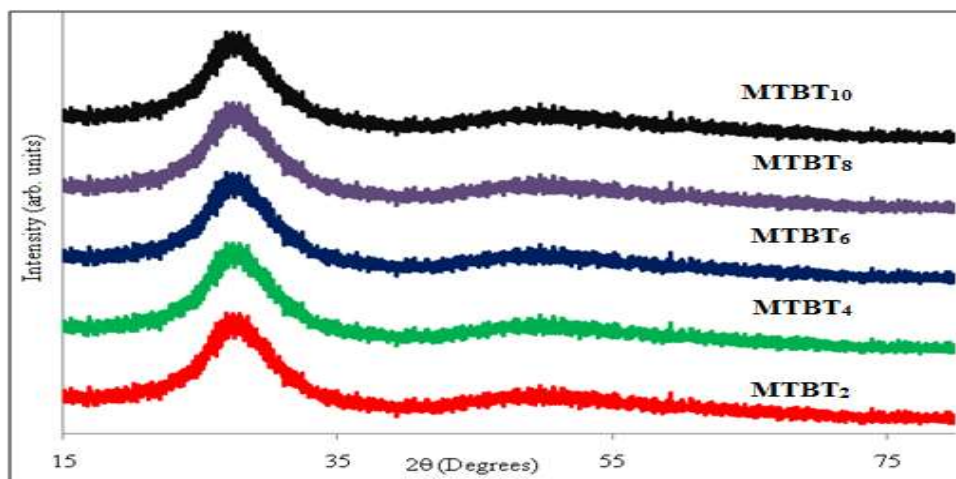


Fig.-1: XRD traces of ZnO-TeO₂-B₂O₃: MnO glasses

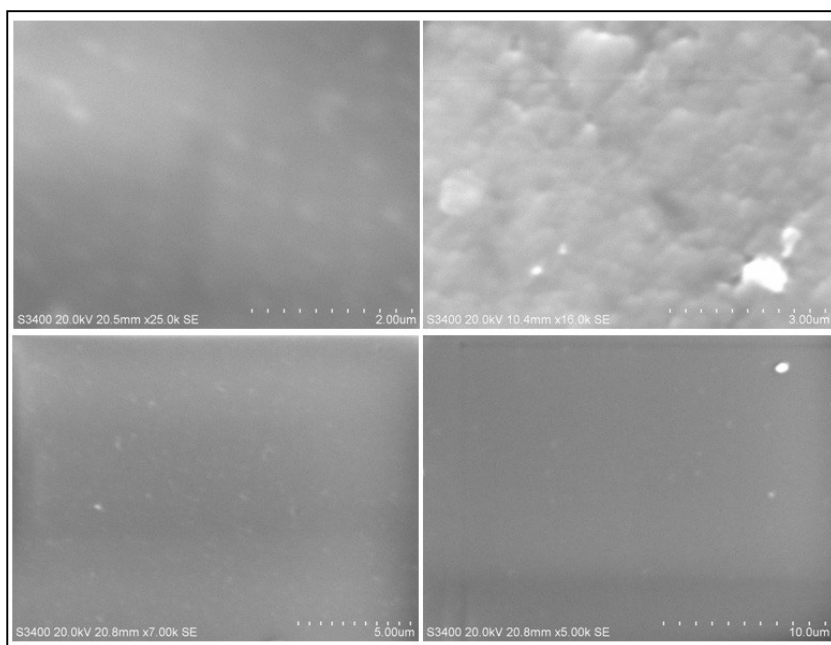


Fig.-2: SEM images of MTBT₂, MTBT₄, MTBT₆ and MTBT₁₀ at 2 μm , 3 μm , 5 μm and 10 μm magnifications respectively (from top left).

Table-1: Experimental physical parameters of ZnO-TeO₂-B₂O₃: MnO glass samples.

Glass	Avg. Mol. Wt.	Density (g/cm ³)	Conc. of 'Mn' ions N_i ($10^{21}/\text{cm}^3$)	Inter ionic distance of 'Mn' ions r_i (\AA°)	Polaron radius r_p (\AA°)
MTBT ₂	96.99	3.988	4.95	0.59	0.24
MTBT ₄	96.82	3.987	9.92	0.47	0.19
MTBT ₆	96.64	3.986	14.90	0.41	0.16
MTBT ₈	96.46	3.984	19.90	0.37	0.15
MTBT ₁₀	96.28	3.983	24.92	0.34	0.14

After thorough examination of physical parameters, dielectric parameters for all the samples were estimated from room temperature to 200 °C. The dielectric characteristics of the MTBT₁₀ sample were analyzed under room temperature conditions and at a frequency of 100 kHz. This sample has shown 11.25 dielectric constant and 0.0126 loss. Upon decreasing the frequency from 100 kHz to 1 kHz and increasing the

temperature, both the dielectric parameters for MTBT₁₀ are increased. Interestingly, the sample containing the highest mol% of MnO demonstrated a dielectric constant value of 13.45 at 1 kHz, which is the maximum value of dielectric constant observed at room temperature. The increase in the above dielectric parameters observed in MTBT₁₀ with a decrease in frequency and increase in temperature could be due to the enhancement in dipolar orientation and ion conduction, respectively.^{3,4,11,12} The highest dielectric constant value observed for the sample MTBT₁₀ could be attributed to the increase in polarization due to the presence of MnO ions. This observation highlights the potential for optimizing the dielectric properties of MTBT₁₀ and other similar materials by adjusting the composition to incorporate suitable ions that can enhance their dielectric constant. The dielectric constant increases up to the maximum value of 9.42 from 7.45, with the prominent rise in the 60 °C - 75 °C range, further exhibiting gradual rise in the dielectric constant is observed for the sample MTBT₂. Changes in Dielectric loss at 10 kHz for all the glass samples with temperature range like dielectric constant were shown in Fig.-4. A slow increase in 'tan δ ' was observed from room temperature to 80 °C following dielectric relaxation effects in the form of peaks associated with the orientation of dipoles were evidenced in between 85 °C to 120 °C. The peak has become broader and more prominent on the high-frequency side and similar trend has been observed with temperature. Similar to the highest dielectric constant exhibited by MTBT₁₀, a maximum value of dielectric loss of 0.0141 was observed at room temperature. On the other hand, the sample MTBT₂ exhibits the smallest value of dielectric loss, with a value of 0.00865 at room temperature. To better understand the dielectric loss in line with frequency and temperature, one sample, MTBT₆, is selected and presented as an inset in Fig.-4. It shows that the dielectric loss decreases with an increase in the investigation frequency. It is also observed that the dielectric loss value increases with an increasing amount of MnO dopant at any temperature and frequency. It is noteworthy that the bump corresponding to dielectric loss appears broad in the temperature range mentioned above, while it was a slight bump in the case of variation of dielectric constant.^{11,12} Moreover, the wide bump shifts towards the higher temperature side as the frequency increases, and similarly, the frequency peak moves towards the higher side against temperature.

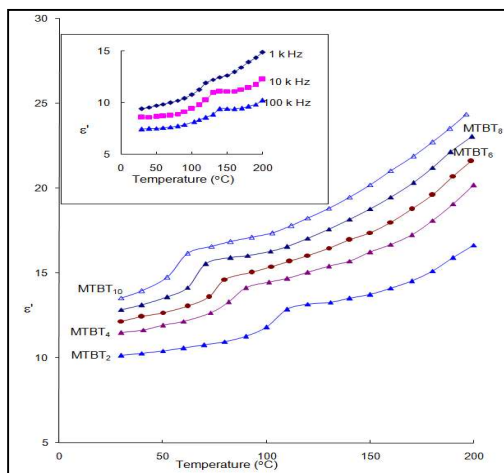


Fig.-3: A comparative graph illustrating the relationship between temperature and dielectric constant, recorded at a frequency of 1 kHz for ZnO-TeO₂-B₂O₃: MnO glass samples. For a particular sample MTBT₂, dielectric constant variation at various frequencies is represented as an Inset.

Table-2 summarizes the dielectric loss maxima and activation energy (AE) for dipoles in electron volts for all the glass samples. The analysis shows that the sample MTBT₁₀ exhibits the highest dielectric constant and loss. Interestingly, it also has the minimum activation energy for dipoles, suggesting that it is easier to polarize this material in an electric field and associated with variation of the band gap. This table indicates that as the average value of maximum dielectric loss (tan δ) increases from MTBT₂ to MTBT₁₀, the activation energy for dipoles decreases from 3.26 eV to 2.24 eV. This indicates that the minimum energy required for the dipole to rotate in an electric field decreases with increasing dielectric loss. Similarly, the activation energy for conduction also decreases from 0.44 eV to 0.27 eV, confirming that energy facilitating conduction of electric current through the sample decreases as the dielectric loss increases.

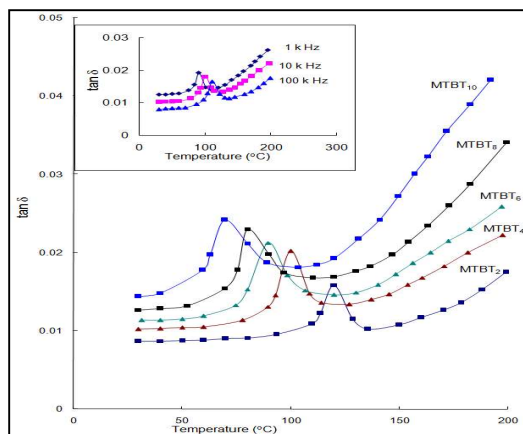


Fig.-4: Comparative representation depicting the temperature-dependent variation of dielectric loss corresponding to the testing frequency of 10 kHz for ZnO-TeO₂-B₂O₃: MnO glass samples. Inset illustrates changes in loss MTBT₈ under three testing frequencies.

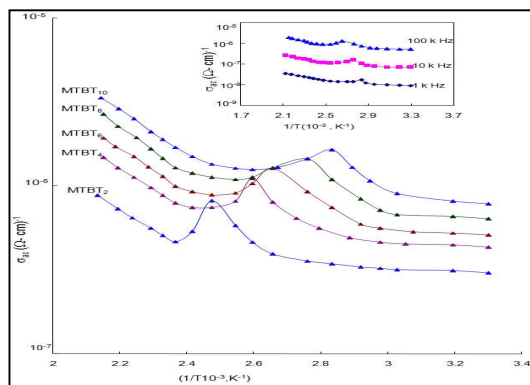


Fig.-5: Variation of σ_{ac} with $1/T$ for ZnO-TeO₂-B₂O₃: MnO Glasses at the Frequency of 100 kHz. Inset Illustrates the Change in a.c. Conductivity with $1/T$ at Different Frequencies for the Glass MTBT₁₀.¹⁰

Table-2: Dielectric Loss Related Parameters for ZnO-TeO₂-B₂O₃: MnO Glass Samples

Sample	(Tan δ_{max}) _{avg}	AE of Dipoles (eV)	AE of Conduction (eV)
MTBT ₂	0.0134	3.26	0.44
MTBT ₄	0.0188	2.65	0.31
MTBT ₆	0.0201	2.51	0.29
MTBT ₈	0.0223	2.37	0.28
MTBT ₁₀	0.0238	2.24	0.27

Overall, the table provides insights into the dielectric behavior of the samples and helps in understanding the relationship between the dielectric parameters. The estimation of the AE for dipoles is performed utilizing the subsequent Eq.

$$f = f_0 \exp \frac{-w_d}{kT} \quad (1)$$

The a.c. conductivity values are evaluated by taking the experimental dielectric constant and loss values pertaining to different temperatures and frequencies using the mathematical relation given below.^{11,12}

$$\sigma_{ac} = \omega \epsilon_0 \epsilon' \tan \delta \quad (2)$$

The relationship between a.c. conductivity, frequency, and temperature are plotted as $\log \sigma_{ac}$ and $1/T$. Based on the above expression, σ_{ac} increases with the presence of MnO at a given frequency and temperature. As per theoretical explanation, the conductivity varies with the product of the dielectric constant and dielectric loss. Consequently, the increasing trend in conductivity mirrors that of the ϵ' and $\tan \delta$. At 100 kHz, the a.c. conductivity for all the samples increases with the presence of trivalent Mn ions, which modify the tellurite

borate glass network (Fig.-5). The presence of these modifier ions creates bonding defects, which allow charge carriers to move. As the content of MnO increases, the number of Mn^{3+} ions also increase, reaching a maximum in the MTBT₁₀ sample. This leads to more space charge polarization in comparison to the other samples, resulting in higher values for the three dielectric parameters discussed earlier. It is worth noting that the zinc and tellurite ions also act as modifier ions similar to trivalent manganese ions, favoring space charge polarization.^{11,12} For a prompt understanding of changes in a.c. conductivity under different temperatures & frequencies for the sample with a high MnO content, shown as Fig.-5. The variation provides dielectric breakdown in a certain region associated with orientation of dipoles.

CONCLUSION

The dielectric constant (ϵ'), loss, and conductivity of ZnO-TeO₂-B₂O₃: MnO glass samples were studied over a frequency range of 1-100 kHz and at temperatures ranging from 30 to 200 °C. The samples prepared using the melt-quenching technique were subjected to characterization through XRD and SEM. Both techniques confirmed that the samples do not possess any crystalline nature and are unstructured. The dielectric constant values exhibit a steady increase with temperature until the temperature range of 60-75 °C, after which sharp increases are observed. The sample with the highest mol% of MnO has the highest dielectric constant measured to be 13.45 at 1 kHz. Moreover, the dielectric loss for all samples gradually increases from 30 - 80 °C, followed by the emergence of dielectric relaxation effects in the temperature range of 85 °C to 120 °C, which are visible as temperature-dependent shifting peaks. At room temperature, the MTBT₁₀ glass sample exhibited a significantly higher dielectric loss value of 0.0141 compared to the other samples. The presence of trivalent manganese ions, which modify the tellurite borate glass network, is responsible for the increasing a.c. conductivity observed in all the samples. The sample MTBT₁₀ has smaller activation energy for dipoles and conduction, indicating a prominent space charge polarization effect. These materials are useful for capacitors, sensors, and several electronic devices.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID IDs, given below:

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