RESEARCH ARTICLE

SAMRIDDHI Volume 14, Issue 4, 2022 Print ISSN: 2229-7111 Online ISSN: 2454-5767

Preparation and Dielectric Investigations of TiO_2 mixed $ZnO\text{-}TeO_2\text{-}B_2O_3$ Glasses

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Abstract

Glasses doped with 0.3 to 1.2 mol% of TiO_2 doped $ZnO\text{-}Sb_2O_3\text{-}B_2O_3$ are synthesized. Samples were tested for their nature by XRD and morphology by SEM pictures. Dielectric constant, loss and a.c. conductivity was measured from temperature 30 to 200°C and frequency range 1 kHz to 100 kHz. The three dielectric parameters were found to rise with the quantity of titanium oxide. The trivalent titanium ions were found to be more in the sample $ZTBT_{12}$ and have shown the highest dielectric constant and loss, however activation energy is small.

Keywords: Titanium; tellurite; borate glasses; dielectric constant; a.c. conductivity.

SAMRIDDHI : A Journal of Physical Sciences, Engineering and Technology (2022); DOI: 10.18090/samriddhi.v14i04.11

Introduction

Preparation and investigations on several glasses are increasing daily as they find a wide range of applications in every sector. Few transition metal oxide glasses gaining attention of many researchers due to their suitability in various aspects like laser hosting materials, non-linear optical materials, optical switching devices etc.[1-3] Among different metal oxide materials viz., Sb_2O_3, TeO_2, Bi_2O_3, tellurium oxide material is selected for the present work as it has wide compositional acceptance range of various d-block elements that may leads to improving their dielectric properties. Most importantly, borate glasses are meant for their ease of synthesis with low cost, moderate melting temperature, high transparency and glass forming ability, and excellent mechanical strength etc. The possible borate groups BO_3, BO_4 and TeO_4 structural units would facilitates the doped metal ions to exhibit desired optical, chemical and electrical properties. From the several investigations, borate glasses play a vital role in many technologically important glasses.[4-6] However, its structure needs to study more when borate oxide mixed with dopant ions aiming at dielectric properties.

TiO_2 was the most favorable oxide mixed with tellurite oxide and borate oxide through well-known TiO_4 and TiO_6 network forming units. Especially TiO_2 doped borate based tellurite glasses can exhibit superior dielectric properties and facilitate them as appropriate materials for solid state ionic devices and storage applications.[7,8] The addition of ZnO to the borotellurite network creates modifying positions that titanium and zinc ions could occupy, creating non-bridging oxygens that led to the increasing structural degree of disorder. A lot of work is carried out to explore the properties of titanium ions in borotellurite glasses and most of such studies were restricted to spectroscopic features; however, very less number of studies have reported dielectric investigations of Ti^{3+} ions, but no studies specifically carried out emphasizing the impact of zinc oxide and tellurite oxides on role of titanium ions in borate and tellurite glass networks.[9,10] This perspective enables the present work to prepare $ZnO\text{-}TeO_2\text{-}B_2O_3$: TiO_2 glasses by melt quenching approach and exploring physical and electrical properties by means of network positions of titanium, tellurite and borate metal ions.

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How to cite this article: Ramesh S, Nagarjuna G, Chandrasekhar B, Raghavaiah BV. (2022). Preparation and Dielectric Investigations of TiO_2 mixed $ZnO\text{-}TeO_2\text{-}B_2O_3$ Glasses. *SAMRIDDHI : A Journal of Physical Sciences, Engineering and Technology*, 14(4), 67-71.

Source of support: Nil

Conflict of interest: None

Experimental Methods

The details of glass constituents with their mol% for the synthesis of glasses in the current investigations are summarized and presented in Table 1 with suitable

Table 1: Nominal composition of glasses (all are in mol. %) chosen for the present study.

Labeling	*Composition particulars (Mol %)*			
	ZnO	*TeO_2*	*B_2O_3*	*TiO_2*
$ZTBT_3$	20	27.7	52	0.3
$ZTBT_6$	20	27.4	52	0.6
$ZTBT_9$	20	27.1	52	0.9
$ZTBT_{12}$	20	26.8	52	1.2

nomenclature. The addition of dopant TiO_2 in place of TeO_2 was possible up to 1.2 mol% only, later, samples lost their transparency.

For the sample preparation TeO_2, H_3BO_3, ZnO and TiO_2 are taken. As per the weight ratio in mol%, all the constituent chemical powders are taken in agate mortar and grinded to smooth powder. Later, taken into platinum crucible that is placed into PID high temperature melting furnace in high temperature 920 to 970°C for 30 to 40 minutes resulting in transparent molten liquid. Meanwhile, brass moulds are arranged to pour the liquid and get desired samples' dimensions. Once samples are ready, and then moved to an annealing furnace maintained at temperature 380 to 420°C to avoid brittle behavior of samples that may occur.

Archimedes' principle is used to determine the densities of samples. Based on experimental densities values, the auxiliary material parameters are calculated to explore the coordination network and substitution modifications. Amorphous nature was tested by using X-ray diffractometer. Surface details and size distribution of grains in the samples were done with the help of scanning electron microscopic images. Dielectric parameters in the frequency 1 KHz to 10 KHz and temperature 30 °C to 200 °C were evaluated using HP Model 4263-B LCR meter.

Results And Discussion

X-ray diffraction scans did not show characteristic sharp peaks of crystalline materials. However, a broad bump appears at an angle of diffraction 2theta = 26° attributes to amorphous nature of glass samples. Figure 1 resembles the same XRD patterns for all test samples and no prominent changes in support of crystalline nature were seen. In agreement with XRD patterns, scanning electron microscopic pictures reveal that there are no clusters, grains with proper boundaries. Thus both XRD scans and SEM images allow us to conclude that all the prepared glass samples do not show any kind crystalline nature that sometimes may be possible due to regular annealing process or gradual cooling treatment. The SEM images of samples $ZTBT_6$ and $ZTBT_{12}$ are given in Figure 2.

As TiO_2 is introduced in place of TeO_2, the average molecular weight found to decreases from 96.93 to 96.21 g/mol. This reduction is fairly understandable as molecular weight of TeO_2 is double that of titanium dioxide. Similarly, very slight decrease in densities from 3.982 to 3.969 g/cm^3 is observed. It might be associated with the fractional addition

Table 2: Experimental physical parameters of ZnO-TeO_2-B_2O_3: TiO_2 glass samples.

Glass	*Avg. Mol. Wt.*	*Density (g/cm^3)*	*Conc. of 'Ti' ions N_i (10^{21}/ cm^3)*	*Inter ionic distance of 'Ti' ions r_i(A°)*	*Polaron radius r_p(A°)*
$ZTBT_3$	96.93	3.982	7.42	0.51	0.21
$ZTBT_6$	96.69	3.978	14.87	0.41	0.16
$ZTBT_9$	96.45	3.973	22.33	0.35	0.14
$ZTBT_{12}$	96.21	3.969	29.82	0.32	0.13

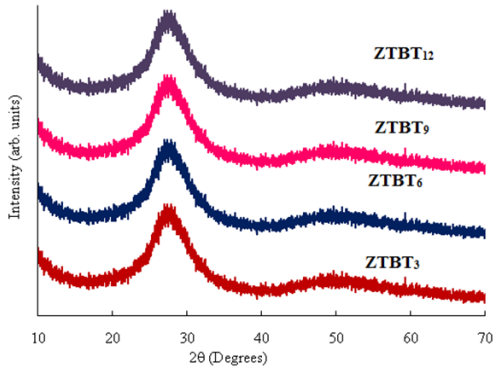

Figure 1: XRD patterns of ZnO-TeO2-B2O3: TiO2 glasses.

of titanium oxide. In the same way, inter ionic distance r_p(A°) and polaron radius r_p(A°) decreased, possibly due to network modifications and coordination symmetry of titanium ions in the borate glass network. Another interesting result is the value of N_i (10^{21}ions/cm^3) increased gradually in proportion to the amount of dopant that is evidenced from Table 2, where the minimum value is 7.42 (10^{21} ions/cm^3) and highest concentration stands at 29.82(10^{21}ions/cm^3). Hence, the increasing addition of titanium oxide is confirmed among $ZTBT_3$, $ZTBT_6$, $ZTBT_9$ and $ZTBT_{12}$.

Dielectric constant and loss of sample $ZTBT_{12}$ at room temperature and frequency 100 kHz are 9.07 and 0.00825 respectively. When frequency is reduced from 100 kHz to 1 kHz, both the values found to increase with rise in temperature. The dielectric constant of sample containing highest mol% of TiO_2 is measured to be 10.95 at 1 kHz and it is the maximum value of dielectric constant at room temperature.[11] Variation of the dielectric constant for all the four samples at 1 kHz frequency in the temperature range 30–200°C are presented in Figure 3. With increase in temperature, the dielectric constant values are steadily increased up to temperature range from 65 to 70°C and after that sharp rises are observed. For better understanding, one sample $ZTBT_6$ is chosen to display the dielectric constant behavior at three frequencies 1, 10 & 100 kHz. From this figure, it is very clear that dielectric constant rises from 6.64 to 8.66 with the reduction in frequency.

Similarly, the variation of dielectric loss of four samples at particular frequency 10 kHz is shown as Figure 4. The

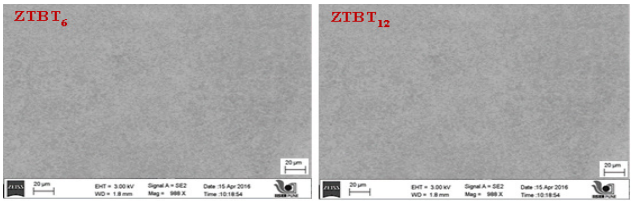

Figure 2: SEM images of ZTBT6 and ZTBT12 glasses.

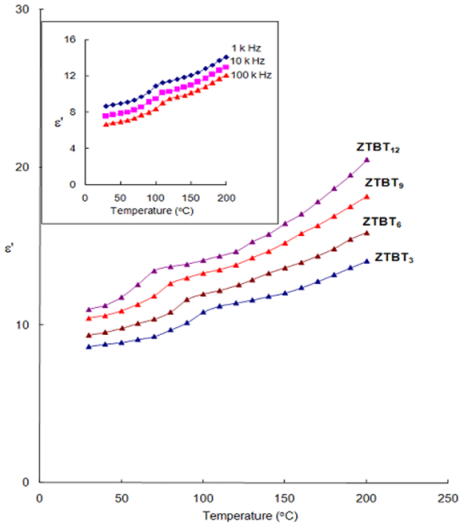

Figure 4: A comparison plot of variation of dielectric loss with temperature measured at 10 KHZ for ZnO-Te O_2.-B_2O_3: TiO_2 glasses. Inset shows the variation of dielectric loss with temperature for the glass sample ZIB T_9 at different frequencies.

loss 'tan δ' also shows same trend as dielectric constant. It gradually increases up to 70°C and later all the samples have exhibited dielectric relaxation effects in the temperature zone 80 to 110°C, which could be seen as temperature-dependent shifting peaks. It is worth mentioning that the broad bump corresponding to dielectric loss appears in the aforesaid temperature range whereas it was slight bump in the case of variation of dielectric constant. The wide bump shifting towards higher temperature side in response to the increasing frequency and similarly the frequency peak moved towards higher side with temperature rise.[12] The sample $ZTBT_{12}$ has shown highest value of dielectric loss of 0.01051 at room temperature in comparison with remaining samples. The dielectric loss of 0.00756 exhibited by $ZTBT_3$ found to be small among all samples at room temperature. For a better understanding of variation of 'tan δ' over increasing frequency from 1 kHz to 100 kHz with respect to temperature, one sample $ZTBT_9$ is chosen. The relevant results are shown as inset in Figure 4. From this graph, it is very clear that the dielectric loss has displayed a decreasing trend with increased investigation frequency. Thus, it allows us to conclude that the dielectric loss value increases with the increasing amount of dopant TiO_2 at any temperature and frequency. The dielectric loss maxima and activation energy for dipoles in electron volts for all the glass samples are evaluated and

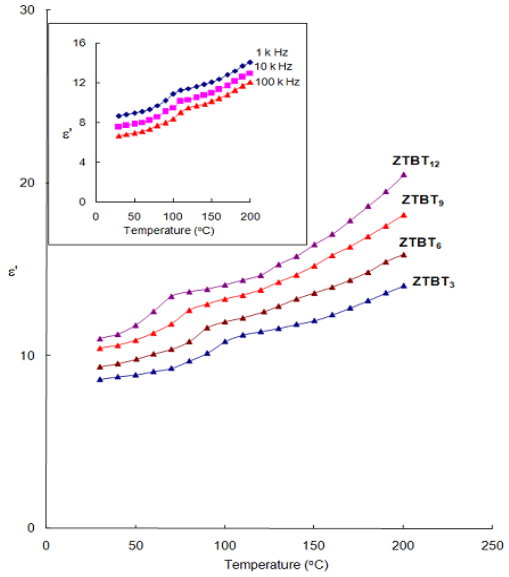

Figure 3: Comparison plot of variation of dielectric constant with temperature measured at 1 kHz for ZnO-TeO2-B2O3: TiO2 glasses. Inset shows the variation of dielectric constant with temperature for the glass sample ZIBT, at different frequencies.

summarized in Table 3. The minimum activation energy for dipoles is observed for the sample $ZTBT_{12}$ as it exhibits highest dielectric constant and loss followed by energy band gap behavior.

The activation energy (A.E.) for dipoles is estimated using the following equation

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

The a.c. conductivity values are evaluated by taking the experimental dielectric constant and loss values pertaining to different temperatures and frequencies using mathematical relation given ahead as:[11,12]

$$\sigma_{ac} = \omega \varepsilon_0 \varepsilon' \tan \delta \quad (2)$$

The a.c. conductivity curves with respect to change of temperatures are plotted as log σ_{ac} and 1/T. As per the above expression, σ_{ac} also increases with TiO_2 at frequency and temperature. Theoretically saying that the conductivity is directly proportional to the product of dielectric constant and dielectric loss, hence it shows an increasing trend as like constant and loss. The variation of a.c. conductivity with 1/T for at a particular frequency of 100 kHz is presented in Figure 5. The increasing a.c. conductivity is seen for all samples associated with trivalent titanium ions that modify the tellurite borate glass network. These modifier ions create bonding defects make charge carriers to move. With the content of TiO_2, the Ti^{3+} ions are increasing and maximum in the sample $ZTBT_{12}$ causing more space charge polarization in comparison with

Table 3: Dielectric loss related parameters for ZnO-TeO_2-B_2O_3: TiO_2 glass samples.

Glass sample	Max. dielectric loss Avg.	A.E.for dipoles (eV)	A.E.for conduction (eV)
$ZTBT_3$	0.0104	2.75	0.38
$ZTBT_6$	0.0119	2.54	0.34
$ZTBT_9$	0.0132	2.38	0.31
$ZTBT_{12}$	0.0148	2.16	0.27

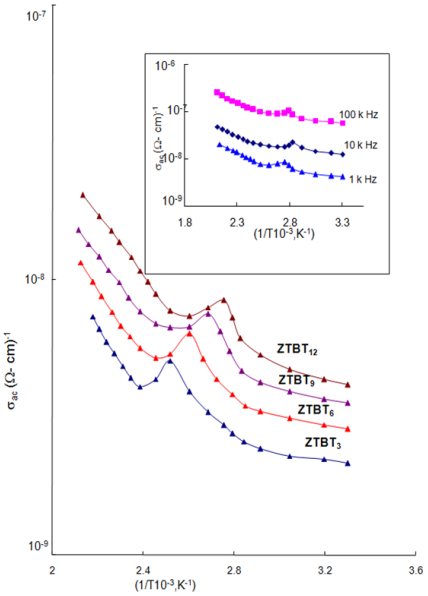

Figure 5: Variation of σac with 1/T for ZnO-TeO2-B2O3: TiO2 glasses at the frequency of 100 kHz. Inset shows the variation of σac with 1/T at different frequencies for the glass ZTBT12.

the remaining samples. Hence above discussed three dielectric parameters are observed to be high for the glass $ZTBT_{12}$. The zinc ions and tellurite ions also act as modifier ions similar to Ti^{3+} ions and favor the space charge polarization.[11,12] To explore the variation of a.c. conductivity with temperature at different frequencies for sample containing high content of TiO_2 is placed as inset of Figure 5.

Conclusion

Dielectric constant ε′, loss tan δ and a.c. conductivities of ZnO-TeO_2-B_2O_3: TiO_2 glass samples are investigated in 1–100 kHz frequency and temperature 30–200°C. Samples prepared by melt quenching technique undergone XRD and SEM. Both the characterization techniques have established the unstructured character and do not show any signs of crystalline nature. With temperature, the dielectric constant values steadily increase up to the temperature range from 65 to 70°C; thereafter, sharp rises are observed. The dielectric constant of sample containing highest mol% of TiO_2 is measured to be 10.95 at 1 kHz which is highest. Similarly, dielectric loss gradually increases up to temperature from 30 - 70 °C and later all the samples have exhibited dielectric relaxation effects in the temperature zone 71 to 110°C which could be seen as temperature dependent shifting peaks. $ZTBT_{12}$ has shown highest value of dielectric loss of 0.01051 at room temperature in comparison with remaining samples. The increasing a.c. conductivity is seen for all the samples that are associated with trivalent titanium ions that modifies the tellurite borate glass network. The A.E. for dipoles and conduction was found to be small for the sample ZTBT12 due to prominent space charge polarization.

References

[1] Marcos, O., Raja, J. A., Andrea S. S. C., & Hellmut, E. (2018). Network former mixing effects in heavy metal oxide glasses: structural characterization of lead zinc phosphotellurite glasses using NMR and EPR spectroscopies. Journal of Physical Chemistry C, 122, 23698–23711.

[2] Marzouk. M. A., Abo-Naf. S. M., Zayed. H. A. & Hassan. N. S. (2017). Glass former effects on photoluminescence and optical properties of some heavy metal oxide glasses doped with transition metal ions. Journal of Applied Spectroscopy, 84, 162–169.

[3] Satyanarayana. T., Valente. M. A., Nagarjuna. G., & Veeraiah. N. (2013). Spectroscopic features of manganese doped tellurite glass ceramics. Journal of Physics and Chemistry of Solids, 71, 229-235

[4] Elkhoshkhany. N., Nora Samir & El Sayed Yousef. (2020). Structural, thermal and optical properties of oxy-fluoroborotellurite glasses. Journal of Materials Research and Technology, 9, 2946-2959

[5] Neelam Berwal, Sunil Dhankhar, Preeti Sharma, Kundu. R. S., Punia. R., & Kishore. N., (2017). Structure Physical, structural, and optical characterization of silicate modified bismuth-borate-tellurite glasses. Journal of Molecular Structure. 1127, 636-644.

[6] Nupur Gupta, Atul Khanna, Hirdesh, Ann-Christin Dippel & Olof Gutowski. (2020). Structure of bismuth tellurite and bismuth niobium tellurite glasses and Bi2Te4O11 anti-glass by high energy X-ray diffraction. Royal Society of Chemistry Advances., 10, 13237-13251.

[7] Fong. W. L., Bashar. Kh. A., Baki. S. O., Zaid. M. H. M. & Mahdi. M. A. (2021). Thermal, structural and optical properties of Bi2O3-Na2O-TiO2-ZnO-TeO2 glass system. Journal of Non-Crystalline Solids, 555, 120621.

[8] Ayuni. J. N., Halimah. M. K., Talib. Z. A., Sidek. H. A. A., Daud. W.M., Zaidan. A.W., & Khamirul A. M. (2011). Optical Properties of Ternary TeO2-B2O3-ZnO Glass System. IOP Conference Service: Materials Science Engineering, 17, 012027.

[9] Çetinkaya Çolak, Sadiye. (2017). Role of titanium ions on the optical and thermal properties of zinc borate glass doped with TiO2. Physics and Chemistry of Glasses – European Journal of Glass Science and Technology Part B, 58, 41-48.

[10] Faznny Mohd Fudzi, Halimah Mohamed Kamari, Amirah Abd Latif, & Azlan Muhammad Noorazlan. (2017). Linear Optical Properties of Zinc Borotellurite Glass Doped with Lanthanum Oxide Nanoparticles for Optoelectronic and Photonic Application, Journal of Nano materials, 2017, 4150802.

[11] Satyanarayana. T., Kityk I. V, et al. Reshak. A. H., & Veeraiah. N. (2009). Role of titanium valence states in optical and electronic features of PbO-Sb2O3-B2O3 glass alloys., Journal of Alloys and Compounds, 482, 283-297.

[12] El Sayed Yousef, El Sayed Mostafa & Amin El-Adawy. (2006). Optical and Electrical Properties of Borate Glasses in the System: B2O3/Na2O/TiO2. Journal of Applied Sciences, 6, 1292-1297.