Effect of zinc oxide on physical and dielectric properties of MnO_2-B_2O_3 glass network

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Abstract: Glass composition ZnO-MnO_2-B_2O_3 containing different contents of ZnO (0, 10, 20, 30, and 40, all in wt. %) were prepared by a popular melt-quenching method. The prepared glasses were characterized by x-ray diffractometry (XRD) and differential thermal analysis (DTA) studies. Infrared (IR) and dielectric studies were also carried out for the prepared glasses. From DTA studies of these glasses, glass forming ability,$K_{gl}$and other stability factors were calculated and presented. From IR studies, variations in intensities of various IR band positions were studied and presented. Parameters, which describe the insulating characteristics, such as dielectric constant, ε, dielectric loss, tanδ, and ac conductivity, σ_{ac}were determined as a function of frequency (10^3Hz to 10^5 Hz) and temperature (30°C to 250°C)and presented from the dielectric analysis of these glasses.

Key words:B_2O_3 glasses, glass forming ability, IR studies, dielectric constant, ε, dielectric loss, tanδ, ac conductivity, σ_{ac}.

1. INTRODUCTION

Glasses are receiving considerable attention due to their unique properties like hardness, good strength, transparency and excellent corrosion resistance. X-ray diffraction (XRD), infrared spectroscopy (IR), differential thermal analysis (DTA) studies has been extensively employed over the years to investigate the structure of glasses [1-4]. Borate glasses, in particular, have been the subject of numerous infrared studies due to their structural peculiarities [5-8]. In pure B_2O_3 glass structure most of the boron is involved in B_3O_6 (boroxol) ring. Addition of modifier breaks boroxol ring and thereby produces BO_3 and BO_4 units [6, 8]. In addition, modifier also changes the physical properties along with structural modifications. B_2O_3 based glasses are very stable against devitrification and are resistance to moisture [9]. Recently, the study of oxide glasses doped with transition metal ions (TMI) has received considerable attention due to their attractive combination of physical and chemical properties. TMI doped borate glasses have application in microelectronics, optical glasses and solid state laser [10-12]. Continued effort for the development of new glassy materials either by doping or by adding TMI, and the study of their novel properties is highly relevant due to their potential applications in various technological applications [13, 14]. Here the preparation, structural characterization, IR and dielectric studies of manganese containing B_2O_3 glass with an intention to precipitate concentrations of ZnO crystal in the borate glass matrix, which may lead to a new composite spintronic material. The modifier oxide chosen to mix in the present glass system, ZnO is thermally stable and appreciably covalent in character. Addition of ZnO in to the glass matrix produce low rates of crystallizations, since ZnO has the ability to form stable glasses due to its dual role; one as glass former and the other is modifier. ZnO as a glass modifier breaks up the continuous borate network and produce more non-bridging oxygen's (NBOs) to depolymerize glass network [15].

In the present study, it is aimed to investigate the influence of different contents of ZnO on physical and insulating characteristics of MnO_2-B_2O_3 glass network by means of dielectric analysis; further, using the results of these studies an attempt has been made to throw some light on the structural modifications, from the data on DTA and IR spectral studies, that take place in the glass network due to varying content of ZnO.

2. EXPERIMENTAL METHODS

Glasses of compositions xZnO-10MnO_2-(90-x)B_2O_3, where, $0 \leq x \leq 40$(all in wt. %), were prepared by melt quenching method [16]. Highly analytical grade reagents (99.9 % pure) $Na_2B_4O_7.10H_2O$, MnO_2 and ZnO were used for the present preparation of glasses. The chosen chemical composition with glass name of present glass systemwas presented in Table 1.

Table 1. Compositions of glasses

Glass Name	Glass Composition
ZMB_0	10Mn_2O-90B_2O_3
ZMB_1	10ZnO-10Mn_2O-80B_2O_3
ZMB_2	20ZnO-10Mn_2O-70B_2O_3
ZMB_3	30ZnO-10Mn_2O-60B_2O_3
ZMB_4	40ZnO-10Mn_2O-50B_2O_3

PID temperature controlled furnace was used for the preparation process of the glasses; melting temperatures of all glasses were found to be in the range of 650-750^{o}C. Annealed glass samples were ground and polished for various studies. Powdered samples obtained by crushing the glass plates were used for x-ray diffraction studies at room temperature by using shimadzu x-ray diffractometer of model XRD–7000S in 2θranges from 10^{o} - 80^{o}. Thedensity d of the glasses was determined by the standard principle of Archimedes' using o-xylene as byuontliquid by using the equation:

$$d=\frac{W_{air}}{W_{liq}}\times d_{oxy} \qquad (1)$$

Where,d_{oxy} represents the density of o-xylene and $W_{air}$and W_{liq} represents weight of the sample in air and weight loss of the sample in o-xylene respectively [17].The refractive index n_d of the glass was measured with an Abbe refractometer at a sodium wavelength of 589.3 nm.Glass transition temperature, T_g, crystallization temperature, T_c, and melting temperature, T_m of glasses were determined by using shimadzu differential thermo gravimetry (DTG) of model DTG-60H with a programmed heating rate of 10 ^{o}C/min. in the temperature range of 30-800 ^{o}C to an accuracy of $\pm$0.1 ^{o}C.FT-IR spectra of the glasses were recorded by using a Perkin Elmer Spectrometer in the wave number range 400-4400 by KBR pellet methodcm^{-1}. The dielectric parameters of the glasses; dielectric constant ε, dielectric loss tan δ and ac conductivity σ_{ac} in the frequency range 10^3-10^5 Hz and in the temperature range 30-250^{o}C were determined from those parameters, which were recorded from LCR Meter (Hewlett-Packard Model-4263B).

3. RESULTS AND DISCUSSION

3.1 Physical Parameters

Different physical parameters of ZnO-MnO_2-B_2O_3 glass materials were calculated and presented in Table 2.

Table 2. Various physical parameters of ZnO-MnO_2-B_2O_3 glasses.

Physical Parameters	ZMB_0	ZMB_1	ZMB _2	ZMB _3	ZMB _4
Average molecular weight, $\overline{M}$	69.571	70.823	71.032	72.094	72.582
Density, d (g/cm^3)	5.623	5.632	5.634	5.645	5.656
Refractive index, n_d	1.553	1.559	1.564	1.568	1.571
Molar volume, V_m	12.372	12.575	12.607	12.771	12.832
Molar refractivity, R_M	1.925	1.975	2.773	2.834	2.849
Reflection loss, R	0.015	0.047	0.048	0.048	0.049

The reflection loss from the glass surface was computed from the refractive index by using the Fresnel's formula:

$$R = \left[\frac{n_d - 1}{n_d + 1}\right]^2 \qquad (2)$$

The molar refractivity R_M for each glass was evaluated using the formula:

$$R_M = \left[\frac{n_d - 1}{n_d + 2}\right]^2 \qquad (3)$$

The molar volume of the glass samples was calculated using the formula:

$$V_M = \frac{\overline{M}}{d} \qquad (4)$$

3.2 XRD Studies

Fig.1 represents the X-ray diffraction patterns of ZnO-MnO_2-B_2O_3 glasses for different contents of ZnO ranging from 0 up to 40 wt. %.

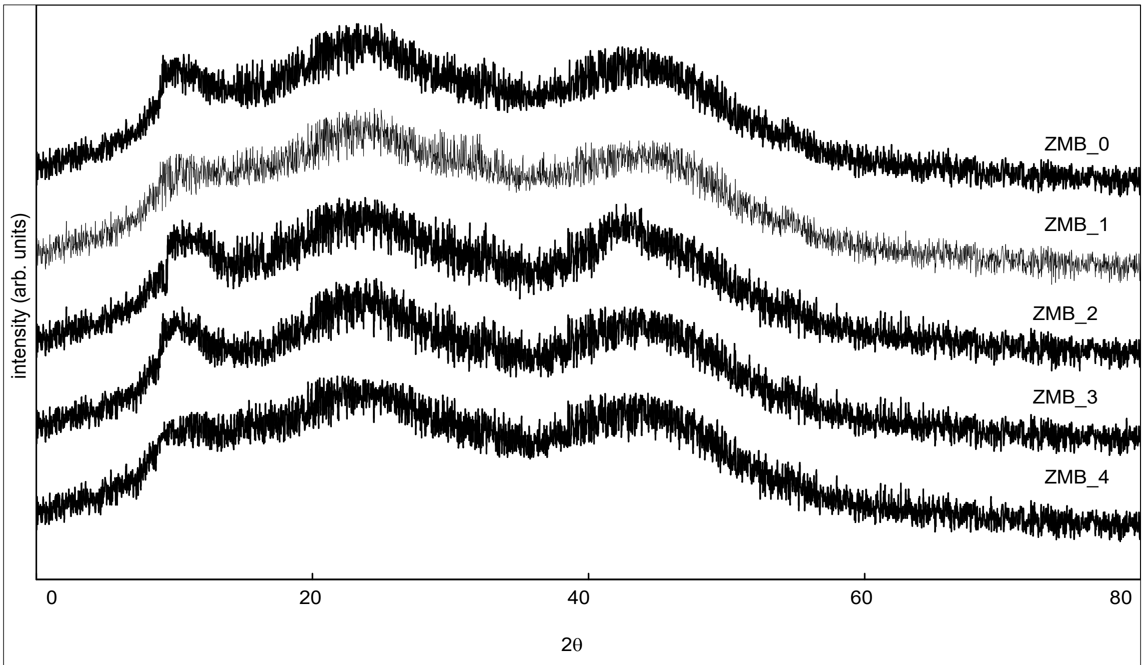

Figure 1. XRD patterns of $ZnO-MnO_2-B_2O_3$ glasses.

As glassy or amorphous materials do not have long-range order, a diffraction pattern containing sharp peak was not expected as observed in crystalline materials. The absence of such sharp peaks in this study confirms the amorphous nature of these glasses.

3.3DTA Studies

Fig. 2 shows the DTA traces of $ZnO-MnO_2-B_2O_3$ glasses. The observed thermograms of the glasses exhibited endothermic and exothermic effect due to various crystalline and non-crystalline phases within the glass network. All glasses exhibited an endothermic change between 250ºC and 279ºC, which can be attributed to the glass transition temperature T_g; the observed T_g of these glasses was found to decrease with increase in ZnOcontent.

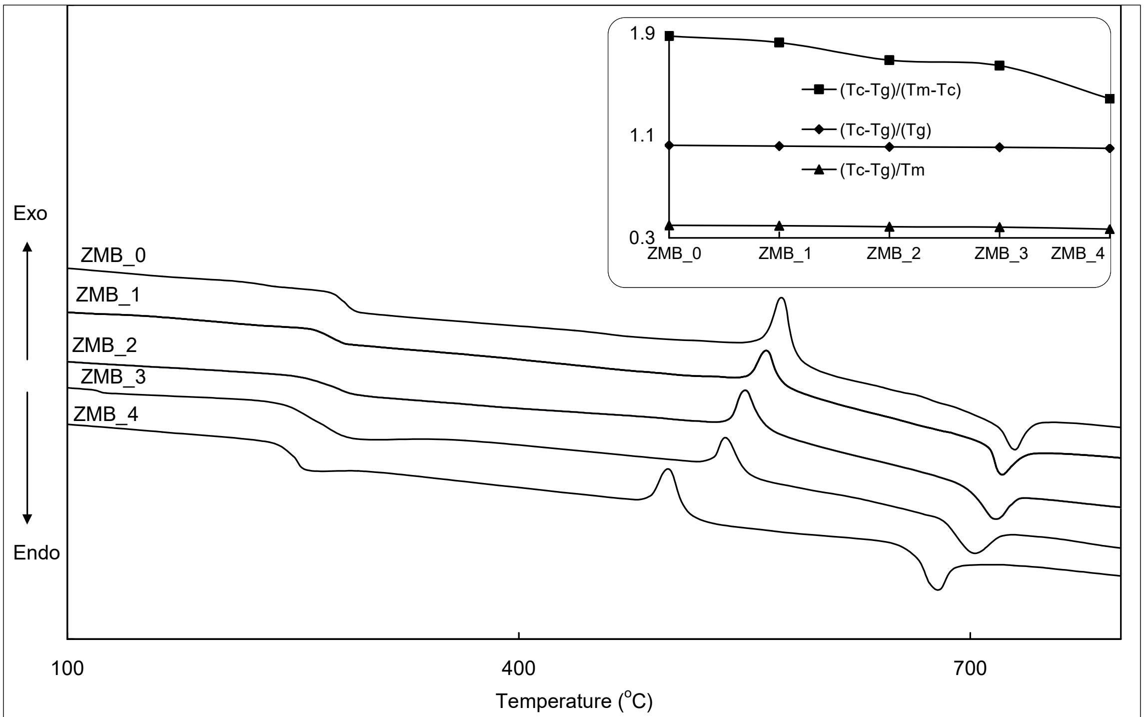

Figure 2. DTA traces of $ZnO-MnO_2-B_2O_3$ glasses. Inset shows the variations of $(T_c-T_g)/T_m$, $(T_c-T_g)/T_g$ and $(T_cT_g)/(T_mT_c)$ with ZnO content.

At still higher temperature T_c, an exothermic peak due to the crystal growth in the range 500°C to 573°C followed by another endothermic effect T_m in the region between 680°C and 728°C due to the re-melting of the glasseswere observed. The observed glass melting temperature T_m of these glasseswas found to reduce with increase in content of ZnO. From the measured values of T_g, T_c and T_m, the parameter, $K_{gl}=(T_c–T_g)/ (T_m–T_c)$, known as Hruby's parameter that gives the information on the stability of the glass networkwas calculated for all glasses. The value of K_{gl}found to decreaseas ZnOcontent increases in the glass network. The variations of various stability parameters, $(T_c\text{-}T_g)/T_m$, $(T_c\text{-}T_g)/T_g$and the Hruby's parameter $(T_c\text{-}T_g)/(T_m\text{-}T_c)$is plotted against ZnO content and presented as an inset in Fig. 2. Table 3presents data on DTA analysis of ZnO-MnO_2-B_2O_3 glasses.The observeddecrease in these parameters may be due to the increase in the number of non-bridging oxygens (NBOs) as the ZnO content increases. The electronic shell of the O^2 ions is affected by the polarizing action of the modifying cation, i.e., Zn^{2+}. Therefore, increasing the ZnO content results in a progressive increase in the number of NBOs, which in turn decreases the number of bridging oxygens [18-20].This obviously suggests that the increased depolymerization of the glass network due to increased modifier action of ZnO with its content increasing from 10 to 40 wt. % in the glass network.

Table 3. Data on DTA analysis of ZnO-MnO_2-B_2O_3 glasses.

Glasses	T_g(°C)	T_c(°C)	T_m(°C)	T_g/T_m	$(T_c\text{-}T_g)/(T_m\text{-}T_c)$	$(T_c\text{-}T_g)/T_g$	$(T_c\text{-}T_g)/T_m$
ZMB_0	279	573	728	0.383	1.897	1.054	0.404
ZMB_1	277	565	725	0.382	1.800	1.040	0.397
ZMB_2	271	551	712	0.381	1.739	1.033	0.393
ZMB_3	265	538	698	0.380	1.706	1.030	0.391
ZMB_4	250	500	680	0.360	1.389	1.000	0.368

3.4 Infrared Spectral Studies

ZnO-MnO_2-B_2O_3 glasses with different contents of ZnO exhibited different IR bands corresponding to borate and ZnO structural groups. Fig.3 shows the IR spectra of ZnO-MnO_2-B_2O_3 glasses recorded at room temperature. The following conventional bands were observed from IR transmission spectra of these glasses.

Band due to ZnO structural unit:

ZnO_4 tetrahedral vibrational units were observed at 455 cm^{-1} for all glasses except for ZnO free glass.

Bands due to Borate structural units:

(a) Band due to bending of B-O-B linkages were observed at 710 $cm^{-1}$for all glasses.
(b) Band due to B-O band stretching of the tetrahedral BO_4 units (Band 1) were observed in the range 840-950 cm^{-1} for all glasses.
(c) Band due to asymmetric stretching relaxation of the B-O of trigonal BO_3 units (Band 2) were observed in the range 1370-1440 cm^{-1} for all glasses.

The observed band positions in the spectra of these samples are similar to those reported for zinc oxide containing various borate glass systems[21].

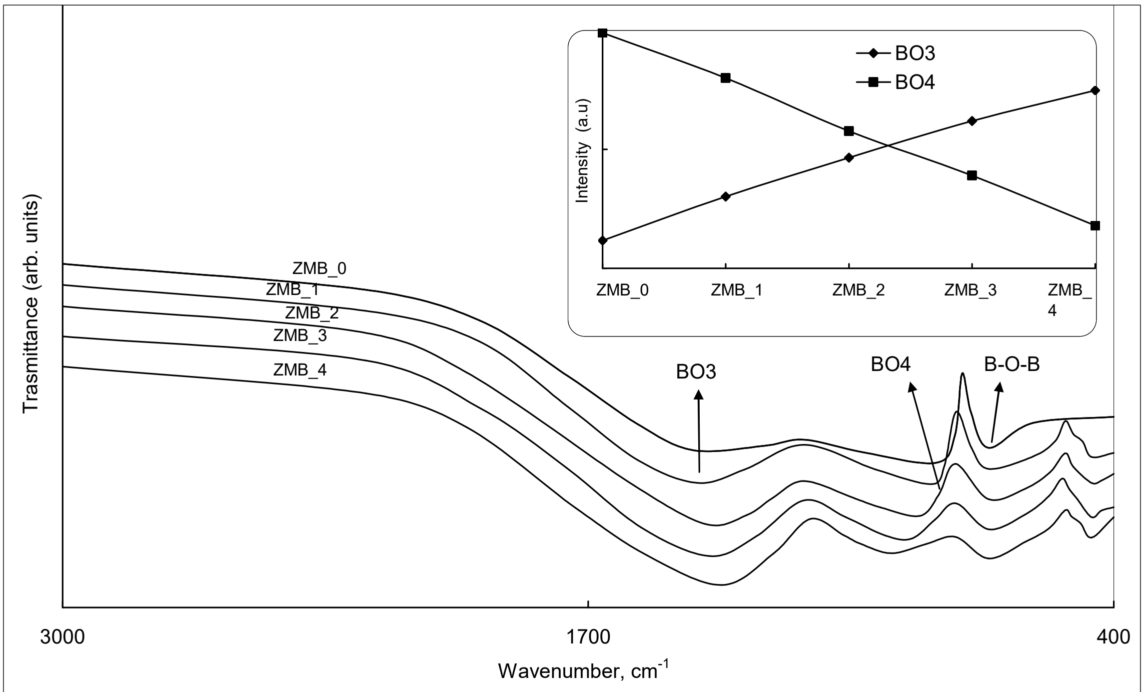

Figure 3. IR spectra of $ZnO-MnO_2-B_2O_3$ glasses. Inset shows variation of band intensities of BO_3 and BO_4 units with ZnO content.

It is well known that the borate network with modifier (ZnO) consists of sp^2 planar BO_3 units and more stable sp^3 tetrahedral BO_4 units. Each BO_4 unit is linked to two such other units and one oxygen from each unit with a metal ion (Zn^{2+}) and the structure leads to the formation of long tetrahedron chains. The study on IR spectral analysis of these glasses revealed that the intensity of band due to BO_4 units is observed to decrease shifting its meta-centre towards slightly higher frequency with the increase of ZnO content from 10 to 40 wt. %.; where as a complete reverse trend is observed for the band due to BO_3 units [22-24]. However, there is no observed change in positions and intensities of bands due to B-O-B linkages and ZnO_4 units.Inset of the Fig. 3 presents the variation of IR band intensities of BO_3 and BO_4 units with increase in ZnO content from 10 to 40 wt. %. These results suggest that the network modification with increased depolymerization in the glass network increases (with creation of more number of non-bridging oxygens, NBO's) with increase in ZnO content from 10 to 40 wt. %. Data on the observed band positions from IR spectra of $ZnO-MnO_2-B_2O_3$glasseswerefurnished in Table 4.

Table 4: Data on IR spectra of $ZnO-MnO_2-B_2O_3$ glasses.

Glasses	BO_3(band 2) cm^{-1}	BO_4(band 1) cm^{-1}	B-O-B cm^{-1}	ZnO_4 cm^{-1}
ZMB_0	1440	840	710	455
ZMB-1	1430	850	710	455
ZMB_2	1410	880	710	455
ZMB_3	1400	900	710	455
ZMB_4	1370	950	710	455

3.5 Dielectric Studies

Fig. 4, 5 and 6, respectively, show the variations of dielectric constant, ε, dielectric loss, tanδ and ac conductivity, σ_{ac} of $ZnO-MnO_2-B_2O_3$glasses with temperature (in the range 30°C to 250°C) measured as a function of different frequencies at 1 kHz, 10 kHz and100 kHz.

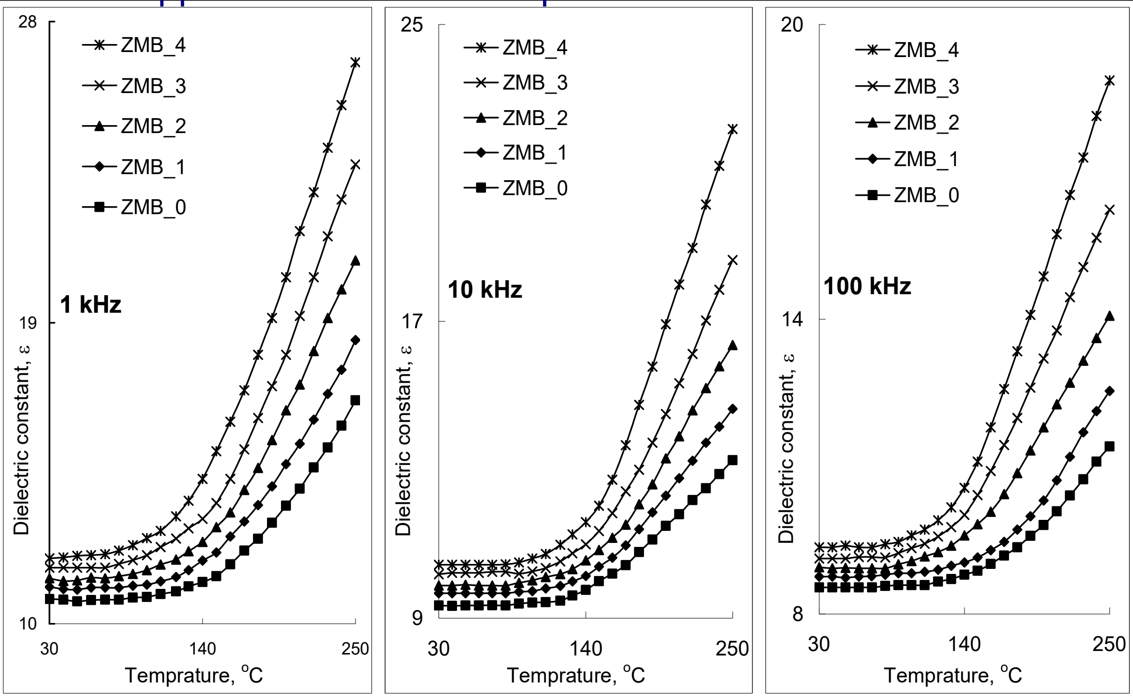

Figure 4. Variation of dielectric constant with temperature at different frequencies for $ZnO-MnO_2-B_2O_3$ glasses.

Dielectric constant, ε is observed to increase with temperature at any frequency for all glasses; in addition, it is observed that the value of dielectric constant increase with increase in ZnO content from 10 to 40 wt. %. However, at any fixed temperature and a particular content of ZnO in the glass network the value of dielectric constant is observed to decrease with increase in frequency (Fig. 4). A similar trend is observed for dielectric loss tanδvariations (Fig. 5).

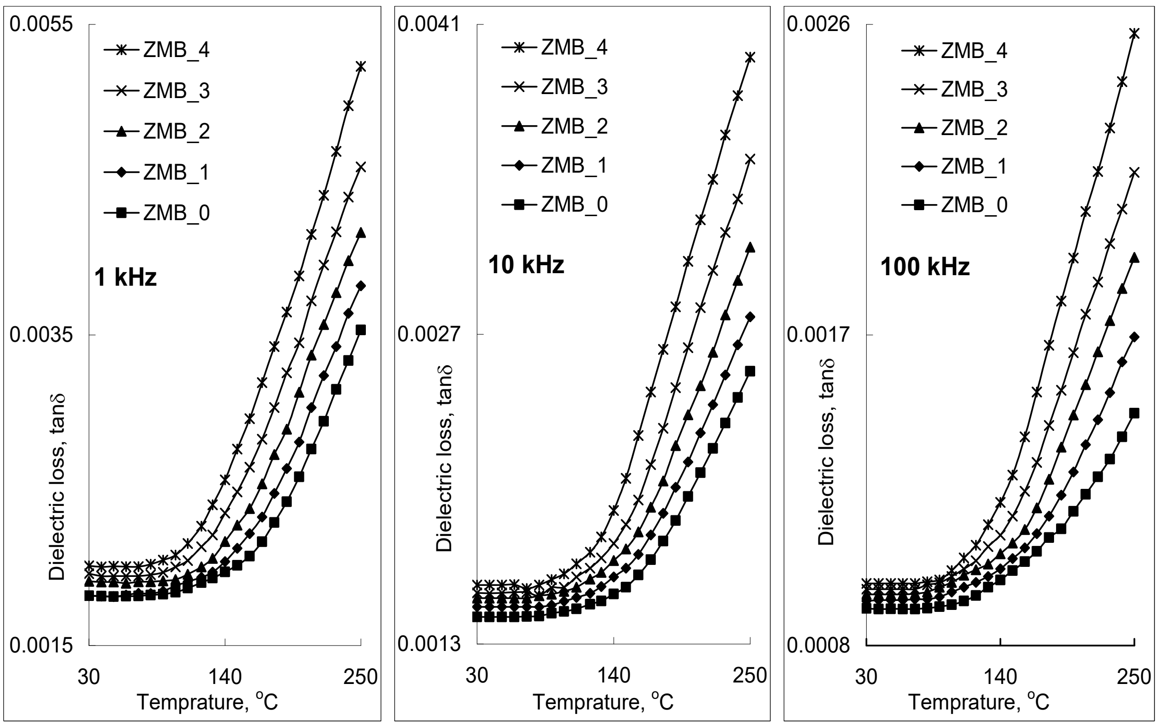

Figure 5. Variation of dielectric loss with temperature at different frequencies for $ZnO-MnO_2-B_2O_3$ glasses.

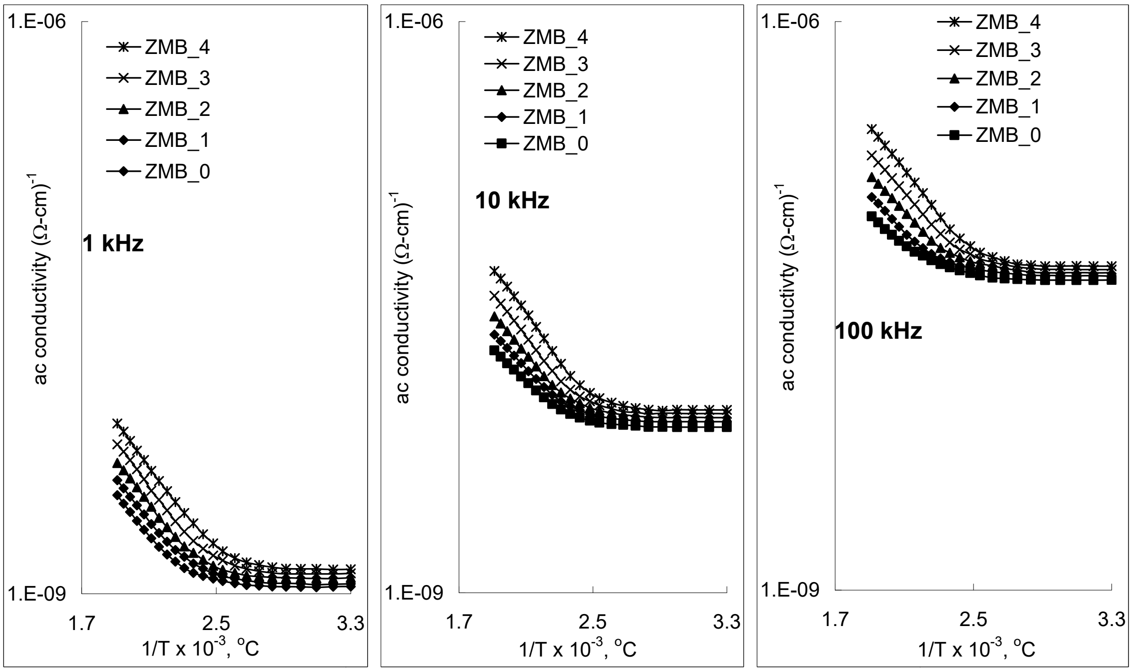

Figure 6. Variation of ac conductivity with reciprocal temperature at different frequencies for $ZnO-MnO_2-B_2O_3$ glasses.

The ac conductivity, σ_{ac} was calculated at different temperatures for these glasses using the equation:

$$\sigma = \omega\varepsilon_o \varepsilon \tan\delta, \qquad (5)$$

(where, ε_o is the vacuum dielectric constant) for different frequencies and the plot of log σ_{ac} against $1/T$ is shown in Fig. 6 for all glasses at different frequencies. σ_{ac} of these glasses is found to increase with temperature and with frequency; in addition, it is observed that σ_{ac} increase with increase in ZnO content from 10 to 40 wt. % (Fig. 6). Similar results were reported for ZnO containing various glass matrices [25-26]. Table 5 present data on dielectric constant ε, dielectric loss tanδ and ac conductivity σ_{ac} of $ZnO-MnO_2-B_2O_3$ glasses for different temperatures at 1 kHz, 10 kHz, and 100 kHz frequencies. Itis well known that electronic, ionic, dipolar and space charge polarizations contribute to the dielectric constant. Among these, the space charge polarization depends on the purity and perfection of glasses. In the present measurements ofε and tanδ of these glasses, an increase of these parameters with increase in ZnO content were noticed due to space charge polarization and due to the bonding defects of these glasses. The defects thus produced, create easy pathways for migration of charges that would build up space charge polarizations leading to an increase in the dielectric parameters, ε and $\tan\delta$ as observed in Fig. 4 and 5, respectively. These variations of such parameters were due to the gradual increase in zinc ions in Zn^{2+} state that act as modifiers in these glasses. σ_{ac} increases as increasing ZnO content indicating the creation of more number of NBOs', which lead to the creation of more number of conduction ions [27-31].

Table 5. Data on dielectric constant, dielectric loss, and ac conductivity of $ZnO-MnO_2-B_2O_3$glasses at 1kHz, 10kHz and 100kHz for temperatures 30°C and 250°C.

Glass	Dielectric constant ε at 1 kHz		Dielectric loss $\tan\delta$ at 1 kHz		ac conductivity σ_{ac} (x $10^{-9}\Omega$-cm^{-1}) at 1 kHz	
	30°C	250°C	30°C	250°C	30°C	250°C
ZMB_0	10.74	16.68	0.0018	0.0035	1.09	3.28
ZMB_1	11.10	18.48	0.0018	0.0038	1.12	3.93
ZMB_2	11.36	20.86	0.0019	0.0041	1.21	4.84
ZMB_3	11.68	23.73	0.0020	0.0045	1.28	6.84
ZMB_4	11.96	26.78	0.0201	0.005	1.34	7.81
	Dielectric constant ε at 10 kHz		**Dielectric loss $\tan\delta$ at 10 kHz**		**ac conductivity σ_{ac} (x $10^{-9}\Omega$-cm^{-1}) at 10 kHz**	
Glass	30°C	250°C	30°C	250°C	30°C	250°C
ZMB_0	9.34	13.26	0.00142	0.0025	7.41	18.75
ZMB_1	9.67	14.64	0.00146	0.0027	7.92	22.71
ZMB_2	9.88	16.36	0.00150	0.0030	8.31	28.25
ZMB_3	10.18	18.65	0.00153	0.0034	8.70	36.35
ZMB_4	10.44	22.18	0.00156	0.0039	9.13	48.93
	Dielectric constant ε at 100 kHz		**Dielectric loss $\tan\delta$ at 100 kHz**		**ac conductivity $\sigma_{\alpha c}$ (x $10^{-9}\Omega$-cm^{-1}) at 100 kHz**	
Glass	30°C	250°C	30°C	250°C	30°C	250°C
ZMB_0	8.54	11.41	0.00090	0.00147	43.28	93.83
ZMB_1	8.76	12.54	0.00092	0.00169	45.43	118.59
ZMB_2	8.95	14.07	0.00094	0.00192	47.36	151.21
ZMB_3	9.13	16.23	0.00096	0.00217	49.10	196.71
ZMB_4	9.36	18.86	0.00098	0.00250	51.21	271.02

4. CONCLUSIONS

In summary, the main conclusions drawn from the results of various studies on ZnO-MnO_2-B_2O_3 glasses are:

Study on DTA analysisshowed the glass forming ability parameterK_{gl}decreased with increase of ZnO content from 10 to 40 wt. %, whichindicatingthat an increased depolymerization with increase in more number of NBOs in the glass network.
IR spectra recorded at room temperature exhibited an increased intensity in band due to BO_3 units at the expense of BO_4 units with increase of ZnO from 10 to 40 wt. %, whichsuggesting that the conversion of BO_4 units to BO_3 units with creation of more number of NBOs in the glass network.
Study on dielectric analysis revealed an observed increasing trend of various dielectric parameters with the content of ZnO from 10 to 40 wt. %, which signifying that the formation of more number of conducting ions due to the creation of more number of NBO's in the glass network.

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