Dielectric properties of NaF–B$_2$O$_3$ glasses doped with certain transition metal ions

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Abstract. Dielectric constant ε, loss tan δ, a.c. conductivity σ and dielectric breakdown strength of NaF–B$_2$O$_3$ glasses doped with certain transition metal ions (viz. Cu^{2+}, VO^{2+}, Ti^{4+} and Mn^{4+}) are studied in the frequency range 10^2–10^7 Hz and in the temperature range 30–250°C. The values of ε, tan δ, $\sigma_{a.c.}$ are found to be the highest for Cu^{2+} doped glasses and the lowest for Mn^{4+} doped glasses. Activation energy for a.c. conduction and the value of dielectric breakdown strength are found to be the lowest for Cu^{2+} doped glasses and the highest for Mn^{4+} doped glasses. With the help of infrared spectra, increase in the values of ε and tan δ of these glasses with frequency and temperature are identified with space charge polarization. An attempt has been made to explain a.c. conduction phenomenon on the basis of quantum mechanical tunneling model (QMT)/carrier barrier hopping model.

Keywords. Dielectric properties; NaF–B$_2$O$_3$ glasses; QMT model.

1. Introduction

The study of dielectric properties such as dielectric constant ε, loss tan δ, a.c. conductivity $\sigma_{a.c.}$ over a range of frequencies and temperatures and the dielectric break down strength of the glasses help in assessing their insulating character. Work along these lines was carried out in recent years on a variety of inorganic glasses by a number of researchers yielding valuable information (Mallawany 1994; Ravi Kumar and Veeraiah 1995, 1998; Ghosh and Chaudhari 1996; Nageswara Rao and Veeraiah 2000).

Alkali fluoro borate glasses are well known due to their variety of applications in phosphors, solar energy converters and in a number of electronic devices. These glasses are relatively moisture resistant, possess high mechanical strength when compared with the conventional alkali oxyborate glasses. Extensive studies on various properties like ESR studies (Sridhar *et al* 1995), optical properties (Sagar *et al* 1998, 1999) and thermoluminescence properties (Ramana and Sastry 1989) of various alkali fluoro borate glasses doped with different transition and rare earth metal ions are available. Quite recently we have reported the results of our studies on various elastic, optical and some insulating properties of lithium, potassium borate glasses doped with certain rare earth ions (Kumar and Veeraiah 1999; Sagar *et al* 1999). These studies have yielded valuable information regarding the mechanical and insulating strength of these glasses. In

this investigation we have attempted to study the various insulating properties like dielectric properties, dielectric breakdown strength of NaF–B$_2$O$_3$ glasses. Interesting changes in the insulating properties of these glasses are expected when they are doped with different transition metal ions like Cu^{2+}, VO^{2+}, Ti^{4+} and Mn^{4+}, in view of the fact that these ions possess different field strengths in NaF–B$_2$O$_3$ glass network. To have a comprehensive understanding over the influence of different transition metal ions on insulating character of sodium fluoro borate glasses, we have undertaken a systematic investigation on dielectric constant ε, loss tan δ and a.c. conductivity σ in the frequency range 10^2–10^7 Hz and in the temperature range 30–250°C and also the dielectric break down strength in the air medium at room temperature.

2. Experimental

For the present investigation, the following compositions of the NaF–B$_2$O$_3$ (all in mol%) were chosen: glass A (pure): 40 NaF–60 B$_2$O$_3$, glass B: 40 NaF–59 B$_2$O$_3$: 1 CuO, glass C: 40 NaF–59 B$_2$O$_3$: 1 V$_2$O$_5$, glass D: 40 NaF–59 B$_2$O$_3$: 1 TiO$_2$ and glass E: 40 NaF–59 B$_2$O$_3$: 1 MnO$_2$. Appropriate amounts of Analar grade reagents of NaF, H$_3$BO$_3$, CuO, V$_2$O$_5$, TiO$_2$ and MnO$_2$ were thoroughly mixed and melted in a platinum crucible at 950°C for about 1 h until a bubble free liquid was formed. The resultant melt was then cast in a brass mould and subsequently annealed at 300°C. The amorphous state of the glasses was checked by X-ray diffraction spectrum recorded on SIEFERT Diffractometer

Model SO DEBYE FLUX-2002. Glass transition temperatures of these glasses were determined from the differential scanning calorimetric studies using TA Instruments DSC 2010 Differential Scanning Calorimeter. The infrared transmission spectra of these glasses in KBr matrices were recorded in the range 200–4000 cm^{-1} using a Perkin-Elmer 1600 IR spectrophotometer. The samples were then ground and finely polished. The final dimensions of the samples were about $1 \times 1 \times 0.2$ cm. The density d of the glasses was determined to an accuracy of 0·001 by standard Archimedes' principle using xylene (99·99% pure) as the buoyant liquid. A thin coating of silver paint was applied (to the larger area faces) on either side of the samples to serve as electrodes. The dielectric measurements were made on LCR Meter (Hewlett-Packard Model-4263B) in the frequency range 10^2–10^5 Hz and on Radart Q-Meter in the frequency range 10^5–10^7 Hz. The dielectric break down strength of all the glasses was determined at room temperature in air medium using a high a.c. voltage break down tester (ITL Model AAH-55) operated with an input voltage of 250 V at a frequency of 50 Hz; it was ensured that all the glasses used for this study were of identical thicknesses.

3. Results

The differential scanning calorimetric recordings from which the glass transition temperatures (T_g) for sodium fluoro borate glasses doped with different transition metal oxides are determined, are shown in figure 1. Figure 2 presents infrared transmission spectra of all the glasses; the spectra show three main groups of bands in the frequency regions 680–710, 800–1200 and 1200–1600 cm^{-1}. Other weak bands observed at various frequencies for these glasses are shown in the same figure. From the measured values of density d and calculated average molecular weight $\overline{M}$, various physical parameters such as dopant metallic ion concentration N_i, mean dopant ion separation distance R_i, and field strength F_i which are useful for understanding insulating character of these glasses are evaluated and presented in table 1.

The dielectric constant ε of pure sodium fluoro borate glasses (40 : 60 mol% of NaF–B$_2$O$_3$) at 30°C and at 10^6 Hz is found to be 7·2 and is almost independent of frequency; when transition metal ions are added into these glasses, ε values at room temperature are found to decrease with increasing frequency (table 2). The dielectric loss (tan δ) variation with frequency at room temperature for all these glasses has also exhibited similar behaviour.

The variation of dielectric constant and loss with temperature at different frequencies for all the glasses show ε and tan δ values increase considerably at low frequencies and in high temperature region; figure 3 presents the variation of dielectric constant with temperature at different frequencies for glass B (Cu^{2+} doped glasses). The comparison of variation of dielectric constant with
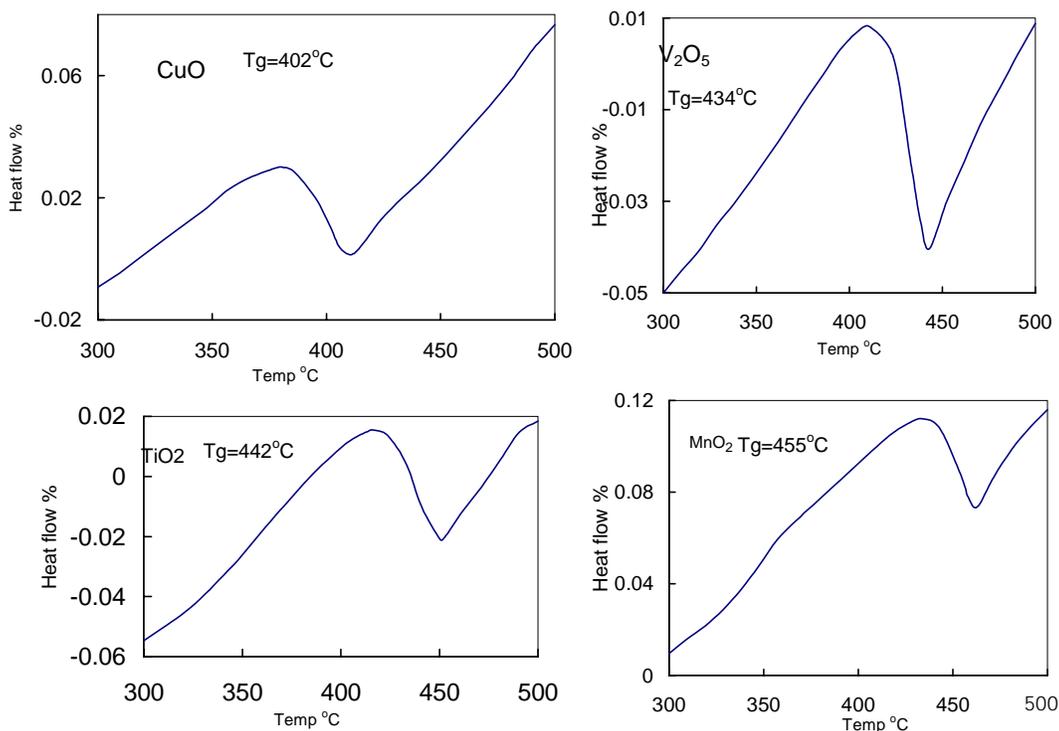
Figure 1.   DSC curves for NaF–B$_2$O$_3$ glasses doped with different transition metal oxides.

temperature for sodium fluoro borate glasses doped with different transition metal ions at 1 kHz is shown in figure 4; the rate of increase of ε with temperature is found to be highest for CuO doped glasses (followed by glasses C, D and E) and lowest for pure glasses. The variation of dielectric loss with temperature has also exhibited similar behaviour; however, the variation of dielectric loss with temperature at different frequencies for glass D is shown in figure 5 and a comparison in figure 6. The summary of

data on the dielectric constant and dielectric loss for all the glasses is presented in table 2.

The a.c. conductivity σ is calculated at different temperatures using the equation

$$\sigma = \omega \varepsilon_0 \varepsilon \tan \delta, \tag{1}$$

(where ε_0 is the vacuum dielectric constant) for different frequencies and the plots of log σ against $1/T$ are shown in figure 7 for glass C and at 100 kHz for all glasses.
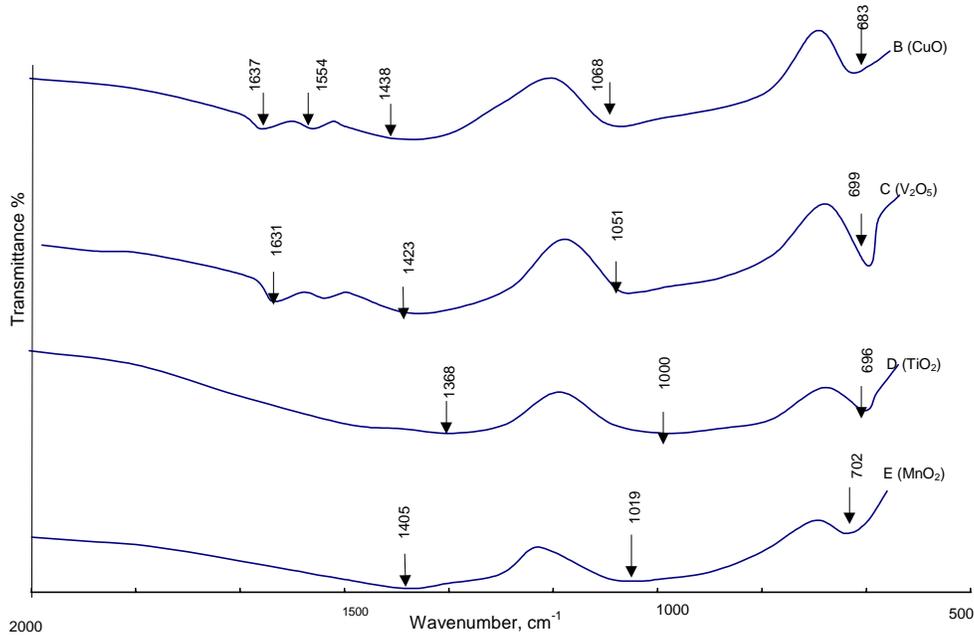
Figure 2. IR spectra of NaF–B₂O₃ glass doped with different transition metal oxides.

Table 1. Various physical properties of NaF–B₂O₃: TMO glasses.

Property	Glass B (Cu²⁺)	Glass C (VO²⁺)	Glass D (Ti⁴⁺)	Glass E (Mn⁴⁺)
Density d (g/cm³)	2·06	2·25	2·28	2·19
Glass transition temp. (T_g,°C)	402	434	442	455
Average molecular weight ($\overline{M}$)	58·66	59·64	58·74	58·67
Doped metal ion concentration N_i (10²² ions/cm³)	2·12	2·21	2·33	2·31
Inter-ionic distance R_i (Å)	3·61	3·55	3·50	3·51
Polaron radius R_p (Å)	1·46	1·43	1·41	1·42
Field strength F_i (10¹⁶ cm⁻²)	0·95	2·43	2·00	1·99

Table 2. Summary of data on dielectric constant and loss.

Glass	ε at 1 kHz		100 kHz		tan δ at 10 kHz ($\times 10^{-3}$)	
	R.T.	250°C	R.T.	250°C	R.T.	250°C
Glass A	8·75	22·86	7·28	12·13	3·7	11·0
Glass B	14·8	56·10	7·90	22·27	8·0	34·0
Glass C	12·5	45·02	7·62	16·00	7·5	28·0
Glass D	11·2	36·20	7·41	13·98	6·5	26·0
Glass E	9·0	30·10	7·32	13·50	6·0	15·0

From these plots, the activation energy for a.c. conduction in the high temperature region over which a near-linear dependence of log σ with $1/T$ could be observed, is calculated and presented in table 3. This activation energy is found to be highest for pure NaF–B_2O_3 glasses and decreases from glass E to B.

4. Discussion

The properties of glasses depend not only on their composition, but also to a considerable degree on their structure.

Deep and important changes in the properties of glass can occur as a result of structural transformation (Ravi Kumar *et al* 1997). NaF–B_2O_3 glasses doped with various metal ions have complex composition and an admixture of network formers and modifiers. B_2O_3 is a well known network former with BO_3 structural units. The presence of BO_4 units is evident in these glasses from the study of the IR spectra. The infrared spectra of NaF–B_2O_3 glasses show three groups of absorption bands as mentioned earlier; (i) in the region 1200–1600 cm^{-1}, due to stretching relaxation of the B–O bond of the trigonal BO_3 units (more specifically $B_3(O_3)^-$ vibrations), (ii) in the region
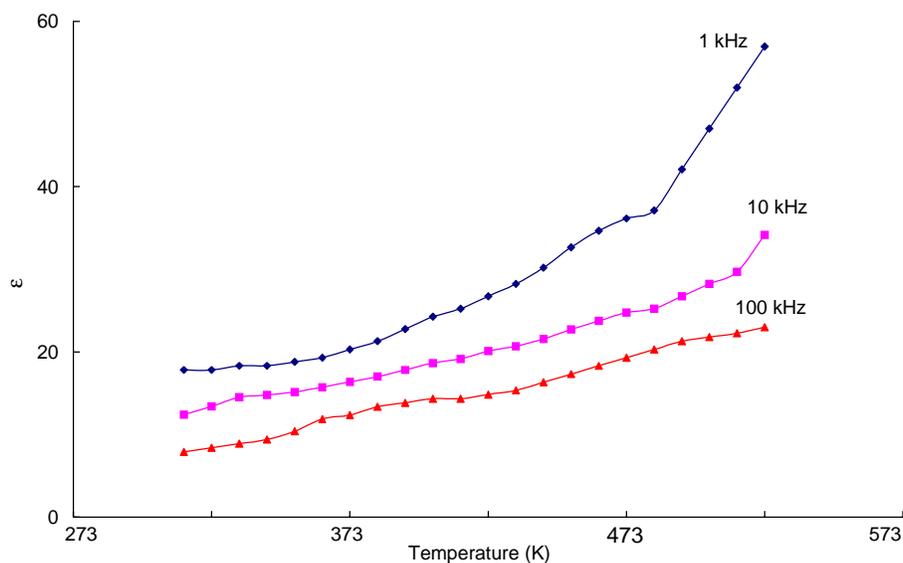
Figure 3. Variation of dielectric constant with temperature at different frequencies for CuO doped NaF–B_2O_3 glasses (glass B).
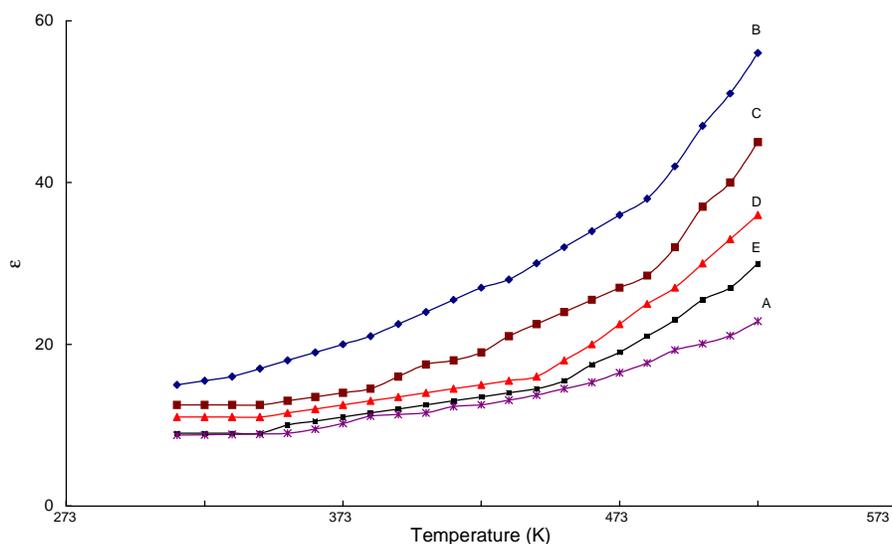
Figure 4. Variation of dielectric constant with temperature at 1 kHz for NaF–B_2O_3 glasses doped with different transition metal oxides: A-Pure, B-CuO, C-V_2O_5, D-TiO_2 and E-MnO_2.

800–1200 cm^{-1}, due to B–O bond stretching of the tetrahedral BO_4 units and (iii) in the region 680–710 cm^{-1} due to the bending of B–O–B linkages in the borate network. When modifier metal oxides are introduced into the glass network the intensity of the bands in the second group is found to be less for CuO doped glasses and highest for MnO_2 doped glasses; further it is also observed that the frequency of this band is shifted towards higher frequencies (clearly seen) from glass C to E. These observations indicate the presence of low concentration of BO_4 units in CuO doped NaF–B_2O_3 glass network (Khalifa and Elhadi 1996; Ahmed and Abd-Elshafi 1998) when compared with the other glasses.

The metal oxide modifiers enter the glass network by breaking up tetrahedral bonds (the oxygen of metal oxides break the local symmetry while metal ions occupy interstitial position) of BO_4 units and introduce coordinated defects known as dangling bonds in these glasses. The increase in the concentration of these bonding defects in the glass network may increase with increase in the size of the dopant ion. This is evidenced from IR spectra as discussed above.

Variation of ε and tan δ with temperature is the highest for glass B in which the modifier present is CuO. This indicates a greater degree of lattice distortion in NaF–B_2O_3 glasses containing CuO among all other glasses and
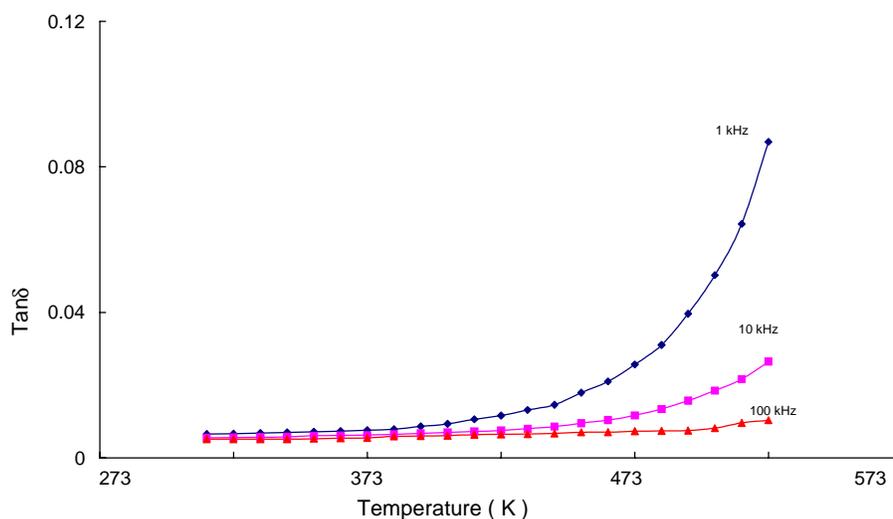
Figure 5. Variation of dielectric loss with temperature at different frequencies for TiO_2 doped (glass D) NaF–B_2O_3 glasses.
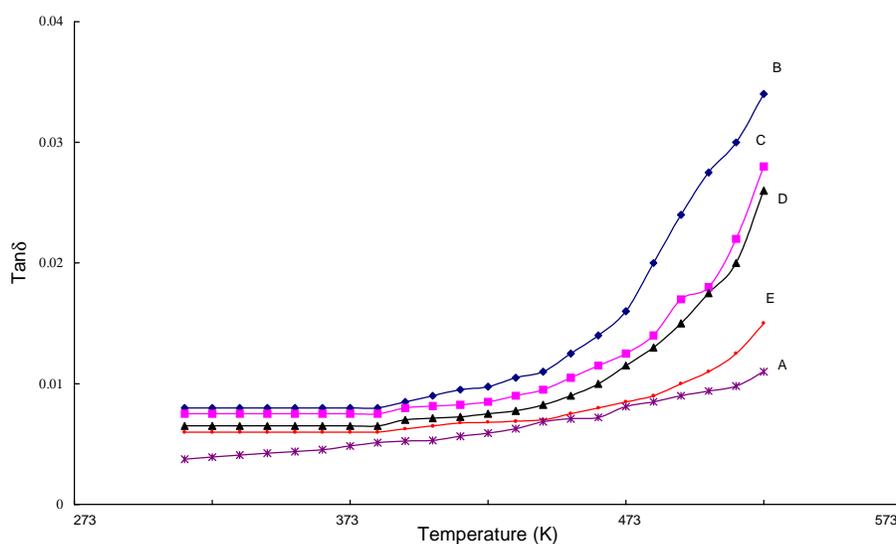
Figure 6. Variation of dielectric loss with temperature at 10 kHz for NaF–B_2O_3 glasses doped with different transition metal oxides: A-Pure, B-CuO, C-V_2O_5, D-TiO_2 and E-MnO_2.

thus resulting in large proportions of space charge polarization, which ultimately causes larger increase of ε and tan δ values as observed when compared with other glasses.

It is interesting to find that the nature of variation of ε and tan δ with temperature is similar. A plot of log ($\Delta\varepsilon$) against $1/T$ (where $\Delta\varepsilon$ is the difference between dielectric constant at any temperature T and that at room temperature) at different frequencies for glass B is shown in figure 9; the graphs are straight lines having about the same slope for all the frequencies in the high temperature region. The computed activation energy is 0·41 eV. This value is practically the same as the activation energy for a.c. conduction in the same temperature region in these glasses. This seems to suggest that the charge carriers responsible for change in ε and σ with temperature in this temperature range are the same. A similar analysis was also carried out on the other glasses and found to yield similar results. Further, this activation energy too is found to decrease from glass E to B (table 3).

In general the a.c. conductivity of the amorphous material where charge carriers experience an approximately random potential energy on diffusing, is found to obey the equation (Austin and Mott 1969):

$$\sigma(\omega) = A\omega^s, \tag{2}$$

(where A is a constant and ω the frequency) with the frequency exponent $s < 1$ up to the frequency of 1 MHz. Though various models have been developed to interpret the a.c. conduction mechanism in the glasses, we have first attempted to explain a.c. conduction in the present NaF–B$_2$O$_3$ glasses on the basis of quantum mechanical tunneling (QMT) model.

According to QMT model, only those pairs of carriers separated by hopping distance R_i, given by:

$$R_i = (1/2\alpha) \ln\left(\frac{v_{ph}}{\omega}\right), \tag{3}$$
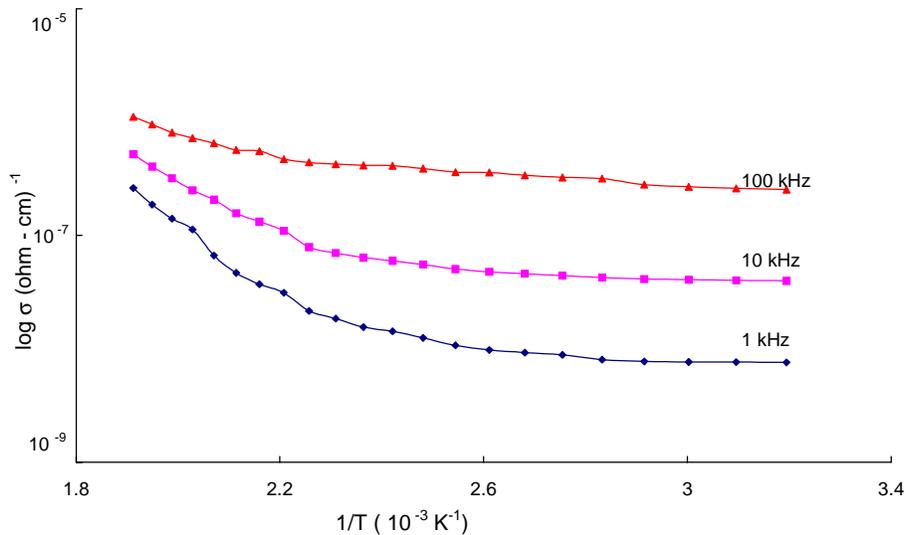
Figure 7. Variation of a.c. conductivity with $1/T$ at different frequencies for NaF–B$_2$O$_3$ glasses doped with V$_2$O$_5$ (glass C).

Table 3. Data on a.c. conductivity of NaF–B$_2$O$_3$ glasses.

| | $N(E_F)$ in (10^{22}, eV^{-1}/cm^3) | | | | A.E. (eV) | | |
| | Austin and Mott | Butcher and Hyden | Pollak | | | | Breakdown strength |
Glass	(1969)	(1977)	(1971)	S_{exp}	$\sigma_{a.c.}$	$\Delta\varepsilon$	(kV/cm)
A	–	–	–	–	0·98	0·97	12·10
B	6·45	2·70	6·50	0·90	0·42	0·41	6·20
C	4·95	2·00	4·99	0·88	0·70	0·71	8·44
D	4·49	1·87	4·50	0·85	0·81	0·80	8·74
E	3·29	1·37	3·30	0·81	0·90	0·91	11·73

The dielectric breakdown strength for pure glass (glass A) is determined to be 12·1 kV/cm; the value of breakdown strength increases from glass B to A (table 3).
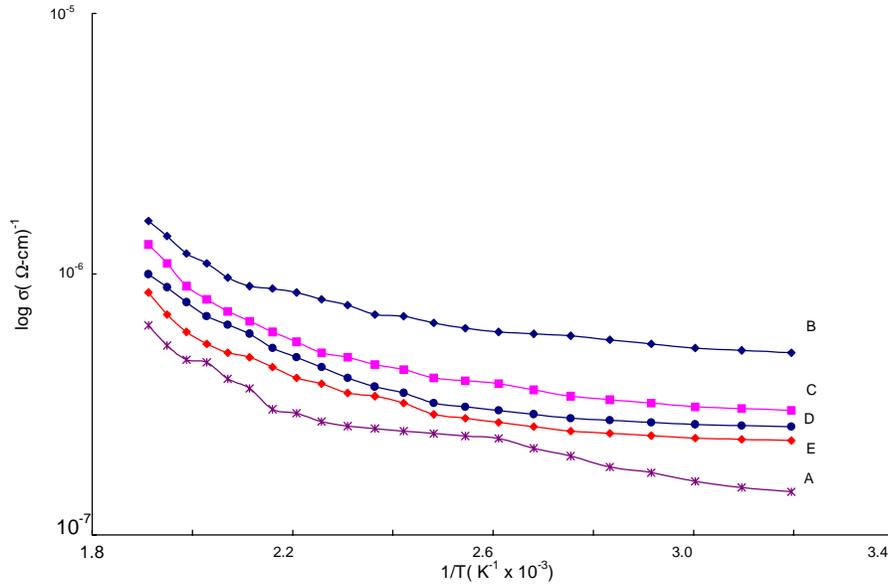
Figure 8. Comparison of variation of a.c. conductivity with $1/T$ at 100 kHz for NaF–B₂O₃ glasses doped with different transition metal oxides: A-Pure, B-CuO, C-V₂O₅, D-TiO₂ and E-MnO₂.
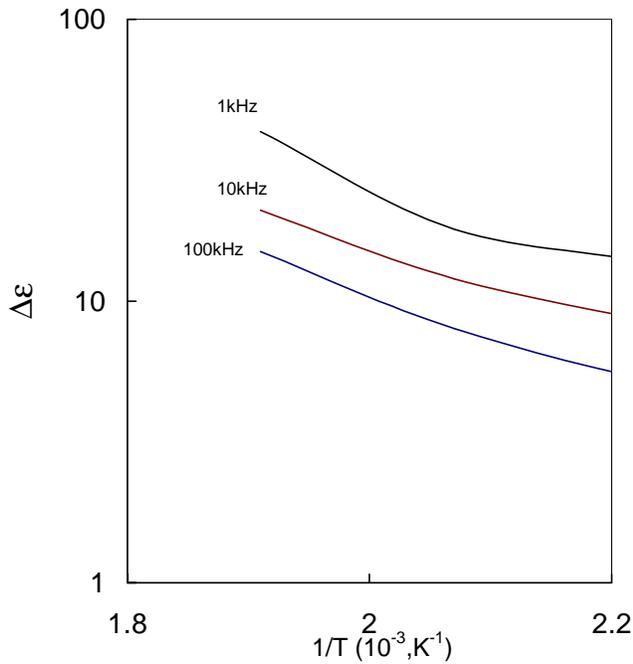
Figure 9. Log $\Delta\varepsilon$ vs $1/T$ at different frequencies for CuO doped NaF–B₂O₃ glasses (glass B).

contribute significantly to the conduction. With this, the equation for a.c. conductivity due to quantum mechanical tunneling is given by:

$$\sigma(\omega) = \frac{\eta e^2 KT}{3}[N(E_F)]^2 \alpha^{-5}\omega\left[\ln\frac{\nu_{ph}}{\omega}\right]^4, \qquad (4)$$

where $N(E_F)$ is the density of the energy states near the Fermi level, α the electronic wave function decay constant, ν_{ph} the phonon frequency and η is a constant and its value is given by: $\eta = \pi/3$ (Austin and Mott 1969), $= 3 \cdot 66\ \pi^2/6$ (Butcher and Hyden 1977), $= \pi^4/96$ (Pollak 1971).

The frequency component s is defined as:

$$s = \frac{\partial(\ln\sigma)}{\partial(\ln\omega)}. \qquad (5)$$

Substitution of (4) into (5) results in

$$s = 1 - \frac{4}{\ln(1/\omega\tau_0)}. \qquad (6)$$

Thus the quantum mechanical tunneling of a carrier through the potential barrier between the sites separated by a distance R_i demands that 's' should be temperature independent.

From the plots of log $\sigma(\omega)$ vs log ω for these glasses at a temperature of 373 K, we have obtained the experimental values of s (table 3); further graphs obtained are straight lines indicating that the exponent s is independent of frequency, hence it is not fully consistent with (6). Perhaps, the more accurate model for a.c. conduction in which s is less dependent on frequency (as observed) for a.c. conduction in NaF–B₂O₃ glasses is the correlated barrier hopping (CBH) model (Elliot 1987) in which the height of the potential barrier is correlated with inter site separation. According to this model

$$s = 1 - \frac{6KT}{E_0 - KT \ln(1/\omega\tau_0)}, \tag{7}$$

where E_0 is the optical band gap. According to (6), the value of s changes by 0·07 for a frequency change of 10^2–10^6 Hz, whereas this change is only 0·003 as per (7) for the same change in the frequency for a fixed optical band gap. Hence (7) can be assumed to give more accurate value of s than (6) for the present glasses and the CBH model can be assumed to be more appropriate than the QMT model for a.c. conduction in these glasses. However, further analysis on a.c. conduction for these glasses is carried out on the basis of QMT model for the lack of accurate value of optical band gap E_0 at different temperatures. The experimental values of s obtained for these glasses are presented in table 3 along with the other important data on a.c. conduction.

Among various mechanisms for conduction (like band conduction, conduction in extended states, conduction in localized states near the band edge and conduction in the localized states near the Fermi level) in the amorphous materials, the conduction in the localized states near the Fermi level occurs when a.c. conductivity is nearly temperature independent and varies linearly with frequency. The conduction in present NaF–B_2O_3 glasses in the low temperature region (up to 400 K) can safely be attributed to take place by this mechanism. The value of $N(E_F)$, i.e. the density of energy states near Fermi level, for a frequency of 10^4 Hz and at 373 K, taking α (determined by plotting log σ against R as per the relation $\sigma \propto e^{-2\alpha R_i}$) $\approx 2\cdot27$ Å^{-1} and $\nu_{ph} \sim 5 \times 10^{12}$ Hz is calculated using (4), with value of numerical constant η suggested by different investigators and presented in table 3. The value of $N(E_F)$ is found to decrease from glass B to E. Further the range of $N(E_F)$ values obtained were $\approx 10^{22}$ eV^{-1}/cm^3. Such values of $N(E_F)$ suggest the localized states near the Fermi level (Elliot 1987). The increase in the conductivity (decrease in activation energy) from glass B to E can be understood due to the increase in the density of these energy states.

A similar conclusion can also be drawn when we look into the glass transition temperatures of these glasses. The glass transition temperature T_g is observed to increase from glass B to E (table 1) and further found to fit into the relation (Tanaka 1985)

$$\ln T_g \approx 1\cdot6\, Z + 2\cdot3, \tag{8}$$

where Z is the average coordination number. This equation indicates that smaller the value of T_g, lower is the value of average coordination number Z. The fact that low value of the glass transition temperature (table 1) observed for CuO doped glasses indicates that the Cu^{2+} ions in NaF–B_2O_3 glass network are loosely bound and hence giving high conductivity (or yielding low activation energy) when compared with the other samples. This may also explain why there is a successive decrease in the

conductivity (or increase in the activation energy for conduction) from glass B to E. When the dielectric is placed in the electric field, the heat of dielectric loss is liberated. If the applied field is an alternating field, the specific dielectric loss i.e. the loss per unit volume of the dielectric, is given by (Tareev 1979)

$$\rho_l = E^2 \,\omega\varepsilon\varepsilon_0 \tan\delta \;\; W/m^3, \tag{9}$$

here E is the electric field applied. This equation indicates that the higher the values of $\varepsilon \tan\delta$ of the glass at a given frequency, the higher are the losses. In a dielectric across which the voltage is applied, heat is liberated, the temperature of the dielectric then rises and the loss increases still more. The dielectric breakdown strength is in fact inversely proportional to the specific dielectric loss represented by (9).

Recollecting the data on breakdown strengths of NaF–B_2O_3 glasses, as seen earlier, the rate of increase of $\varepsilon \tan\delta$ with temperature is highest for glass B and minimum for pure glass (glass A). Though the breakdown strengths are actually determined at room temperature, the heat liberated during the breakdown rises the temperature of the glass and hence rises the $\varepsilon \tan\delta$ value. Since the rate of increase of $\varepsilon \tan\delta$ with temperature is highest for glass B, the breakdown strength is lower when compared with the other glasses. Thus the experiments on the dielectric breakdown strength of NaF–B_2O_3 glasses reveal that there is a large concentration of defects (such as dangling bonds and point defects) in CuO doped glasses when compared with the other glasses. Further, it may be noted here that among all the metallic ions doped in these glasses Cu^{2+} ion has the highest ionic radius (0·072 nm) which may be the reason for the presence of large concentration of defects in these glasses.

5. Conclusions

From the results of various electrical measurements on NaF–B_2O_3 glasses doped with CuO, V_2O_5, TiO_2 and MnO_2, it is observed that there is a larger increase in the rates of $\varepsilon \tan\delta$, $\sigma_{a.c.}$ with temperature and decrease in the values of dielectric breakdown strength and activation energy for a.c. conduction for the glasses containing different transition metal ions.

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