Dielectric properties of LiF–B$_2$O$_3$ glasses doped with certain rare earth ions

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Abstract. Dielectric constant ε, loss tan δ and a.c. conductivity σ of LiF–B$_2$O$_3$: Ln^{3+} (where Ln = Ce, Pr, Nd and Tb) glasses are studied as functions of frequency (in the range 10^2–10^6 Hz) and temperature (range 30–200°C). The dielectric breakdown strength of these glasses was also determined at room temperature in an air medium. The rate of increase of ε and tan δ with temperature decreases with decrease in the ionic radius of RE^{3+} ion whereas the dielectric breakdown strength, the activation energy for a.c. conduction in the high temperature region decreases with increase in the ionic radius of RE^{3+} ion. An attempt has been made to explain the a.c. conduction in these glasses on the basis of quantum mechanical tunnelling (QMT) model.

Keywords. Dielectric properties; LiF–B$_2$O$_3$ glasses; rare earth ions; QMT model.

1. Introduction

The study of dielectric properties such as dielectric constant ε, loss tangent tan δ and a.c. conductivity σ over a wide range of frequencies and temperatures, and also the dielectric breakdown strength of these glasses helps 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 (El Kholy 1984; Hampton *et al* 1988; Mallawany 1994; Ravi Kumar *et al* 1997; Ravi Kumar and Veeraiah 1998). LiF–B$_2$O$_3$ glasses are known for their applications in phosphors, solar energy converters and in a number of electronic devices. Doping of Ce^{3+} ions in LiF–B$_2$O$_3$ glasses makes them good photosensitive materials, whereas the doping of other rare earth ions such as Pr^{3+}, Nd^{3+}, Tb^{3+}, etc makes these glasses good laser materials. Thus to throw some light on the insulating character and the mechanism of electrical conduction in these glasses, their dielectric properties were studied. Although some studies on physical properties of lithium borate glasses are available, most of them are restricted to lithium oxyborate and some other halo borate glasses like LiCl–B$_2$O$_3$, LiI–B$_2$O$_3$ glasses (Soppe and Den Hartog 1989; Shue and Tuller 1990; Znasik and Sasek 1990). A few investigations are available on LiF–B$_2$O$_3$ glasses doped with some rare earth ions as such, but they are restricted to ESR studies etc (Sridhar *et al* 1995). We report the results of our studies on dielectric properties

such as dielectric constant ε, loss tangent tan δ and a.c. conductivity σ in the frequency range 10^2–10^6 Hz and in the temperature range 30–200°C, and also the dielectric breakdown strength at 30°C in the air medium.

2. Experimental

For the present study, four rare earth ions (Ce^{3+}, Pr^{3+}, Nd^{3+} and Tb^{3+}) with successive decrease in the ionic radii are chosen for doping in LiF–B$_2$O$_3$ glasses. The detailed compositions of these glasses are: Glass A: 40 LiF–59 B$_2$O$_3$–1 CeF$_3$; glass B: 40 LiF–59 B$_2$O$_3$–1 PrF$_3$; glass C: 40 LiF–59 B$_2$O$_3$–1 NdF$_3$; glass D: 40 LiF–59 B$_2$O$_3$–1 TbF$_3$.

As mentioned above, doping of Pr^{3+}, Nd^{3+} and Tb^{3+} ions in the present LiF–B$_2$O$_3$ host glasses makes these glasses as laser materials. When we undertook fluorescence studies on these glasses with different dopant concentrations (Ravi Kumar 1996), we observed that the lasing transitions, for e.g. $^3P_0 \rightarrow {}^3H_4$ in Pr^{3+} glasses and $^5D_4 \rightarrow {}^7F_5$ in Tb^{3+} glasses, were found to show maximum branching ratios and high intensities when the dopant concentration was around 1 mol%. On the basis of this, the concentration of dopants for the present dielectric measurements is also taken as 1 mol% although some measurements at room temperature are taken with different dopant concentrations. Appropriate amounts (all by mol%) of Analar grade reagents of LiF, H$_3$BO$_3$ and LnF$_3$ were thoroughly mixed and melted in a platinum crucible at 900°C for about an hour until a bubble-free liquid was formed. The resultant melt was poured on a brass mould

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Table 1. Some physical properties of LiF–B$_2$O$_3$: Ln^{3+} glasses.

Property	Glass A (Ce^{3+})	Glass B (Pr^{3+})	Glass C (Nd^{3+})	Glass D (Tb^{3+})
Ionic radius of RE^{3+} ion present in the glass (Å)	1·180	1·160	1·150	1·090
Density, d (g/cc)	2·115	2·129	2·143	2·216
Average molecular weight (M)	73·930	73·940	73·980	74·120
RE^{3+} ion conc. N_i (10^{22} ions/cc)	1·723	1·734	1·745	1·800
Inter ionic distance of RE^{3+} ions (Å)	3·871	3·863	3·855	3·811
Glass transition temperature (T_g °C)	428	442	449	450
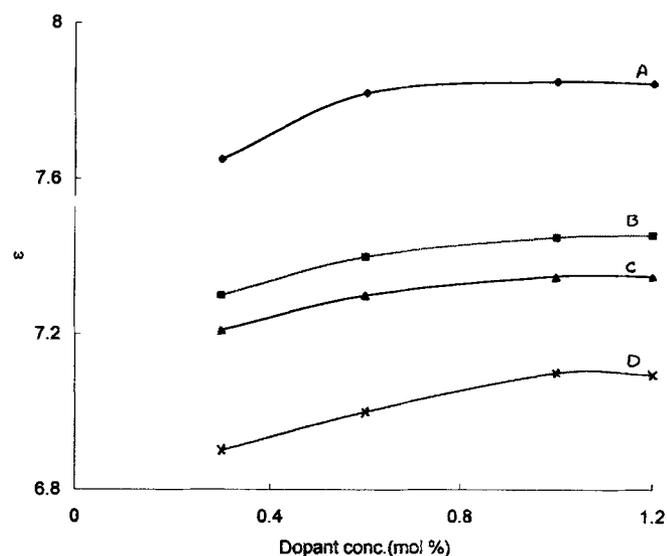
Figure 1. Variation of dielectric constant ε at room temperature with dopant concentration at 500 Hz.

and subsequently annealed at 300°C. The amorphous state of the samples was checked by X-ray diffraction spectra recorded on a Siefert Diffractometer model SO-Debye Flux 2002 with copper target and nickel filter operated at 40 kV and 30 mA. The samples were then ground and finely polished. The approximate dimensions of the samples used for the present measurements were 1·0 × 1·0 × 0·1 cm^3. A thin coating of silver paint was applied (to the larger area faces) on either side of the samples to serve as electrodes.

The capacitance measurements were made on a GR 1615A Capacitance Bridge in the frequency range 10^2–10^5 Hz and on a Radart Q-Meter Model 1202 between 10^5–10^6 Hz. Dielectric breakdown strength for all these glasses was determined at room temperature in air medium using a high a.c. voltage breakdown tester (Dot Tech Model Dot-452) 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

Some physical parameters like average molecular weight, M of the glass, RE^{3+} ion concentration N_i, inter ionic distance r_i of RE^{3+} ions in the glass which are useful for understanding the dielectric properties of LiF–B$_2$O$_3$ glasses are evaluated and presented in table 1 together with the glass transition temperatures.

As a preliminary study, we measured the dielectric constant (figure 1) and dielectric loss of these glasses with different dopant concentrations at room temperature (≈ 30°C) at a fixed frequency of 500 Hz. As the concentration of dopant increased, the dielectric constant and dielectric loss were found to increase for all the glasses nearly up to the concentration of 1 mol%; further increase in the dopant concentration did not show any significant changes in the dielectric constant (figure 1) and dielectric loss. Hence we have chosen 1 mol% as the dopant concentration for dielectric measurements of these glasses.

The dielectric constant ε of CeF$_3$ doped glass (i.e. glass A) at room temperature (≈ 30°C) and at 10^6 Hz was 7·4 and was found to increase with decrease in frequency (figure 2), while the ε values at room temperature were found to decrease gradually at a fixed frequency from glass A to D (figure 2). The dielectric loss (tan δ) variation with frequency at room temperature for all the glasses also exhibited similar behaviour.

The variation in the dielectric constant with temperature at different frequencies for glass A is shown in figure 3; ε increased slowly up to about 100°C, beyond this temperature ε rose rapidly and was found to be highly frequency-dependent, showing larger values at lower frequencies. A similar behaviour was exhibited by ε with temperature for all other glasses. However, for all the glasses a comparison of the variation of ε with temperature

at 2×10^3 Hz is shown in figure 4. It was observed that the rate of increase of ε with temperature was highest for glass A and lowest for glass D. The variation of dielectric loss $\tan \delta$ with temperature at different frequencies for glass B is shown in figure 5 and for all the other glasses at 10^3 Hz is shown in figure 6; these curves exhibit similar behaviour as that of dielectric constant ε with temperature.

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 $\log \sigma$ against $1/T$ are shown in figure 7 for glass C and for all the other glasses at
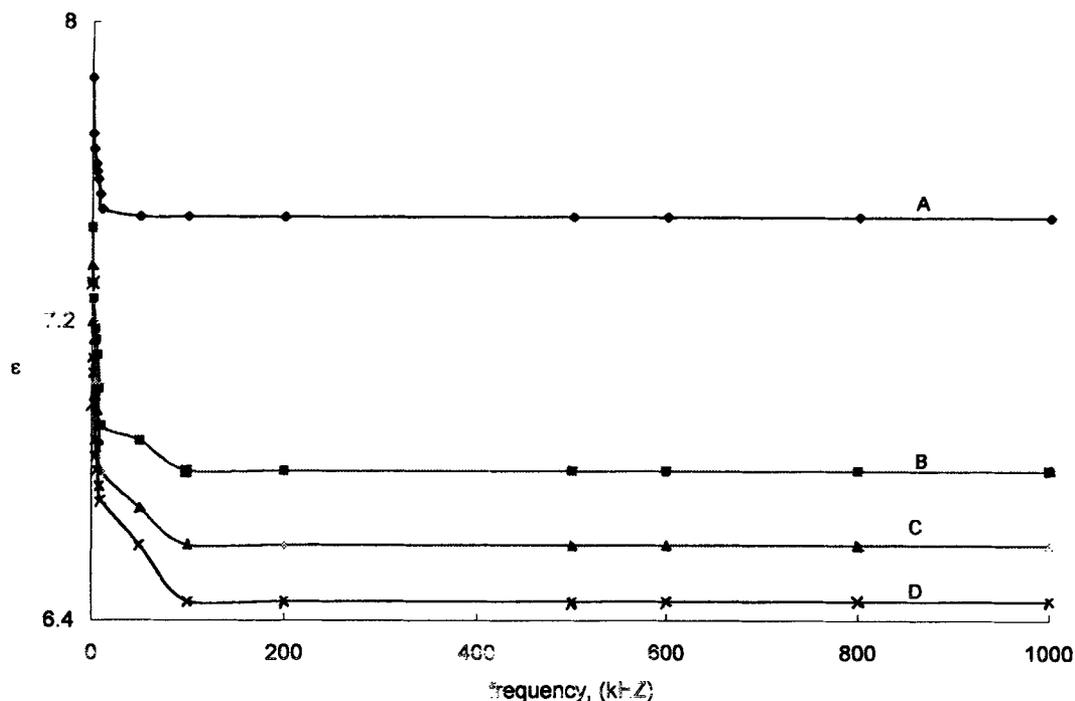

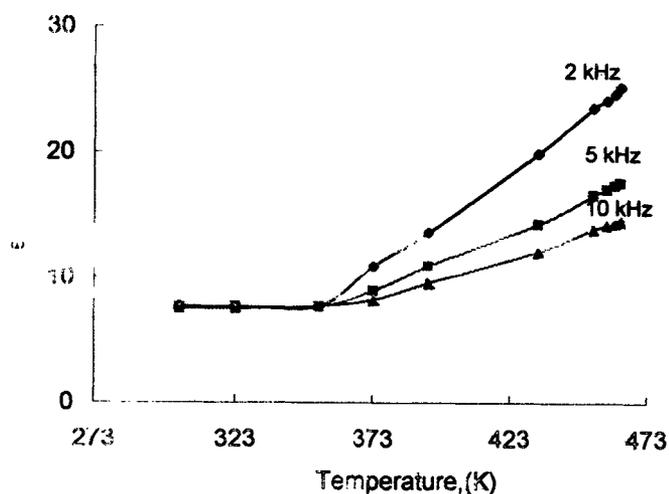**Figure 2.** Variation of dielectric constant ε with frequency for all the glasses at room temperature.

Figure 3. Variation of dielectric constant ε with temperature at different frequencies for glass A.
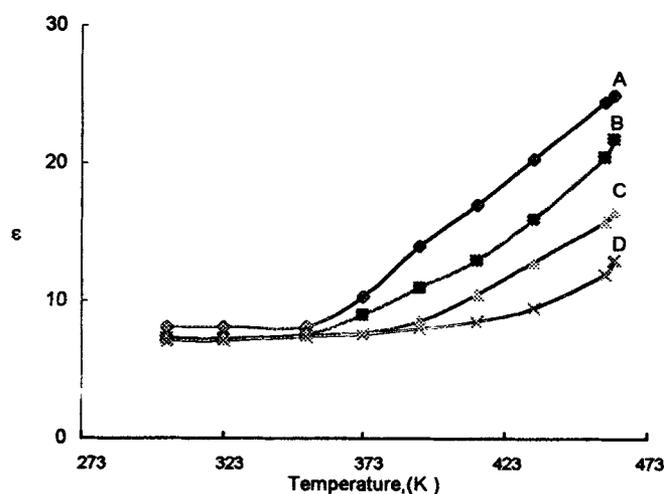

Figure 4. Variation of dielectric constant ε with temperature at 2 kHz for all the glasses.

10^4 Hz in figure 8. From these plots, the activation energy for conduction in the high temperature region over which a near-linear dependence of $\log \sigma$ on $1/T$ could be observed, is calculated and presented in table 2 along with the other pertinent data on a.c. conduction. This activation energy is found to be minimum for CeF_3-doped glasses and increases with decrease in the ionic radius of RE^{3+} ion dopants.

The dielectric breakdown strength of glass A is 13·4 kV/cm; this value increases as we go from glass A to glass D (table 2).

4. Discussion

In general, the properties of glass depend upon its composition and to a considerable extent upon its structure. Lithium fluoro borate glasses doped with LnF_3 have complex composition and are an admixture of network formers and modifiers. B_2O_3 is a well-known network former and LiF is a network modifier which enters the B_2O_3 glass network by breaking up the B–O bonds (the fluorenes of LiF break the local symmetry while Li^+ ions occupy interstitial positions) and introduces co-ordinated defects known as dangling bonds or it may even cause an increase in coordination of boron from 3 to 4 thus creating BO_4 units. Earlier electron spin resonance and optical absorption experiments (Shelby 1994; Sridhar *et al* 1995) indicated that the rare earth ions, when they are present in the glass matrices impose virtually no specific, or narrowly defined, site preference in the glass network. But there are reports (Shelby 1994) which suggest, that rare earth ions also enter the glass network as modifiers by breaking up the random network, thereby leaving the nonbridging oxygens in the B_2O_3 glass lattice.
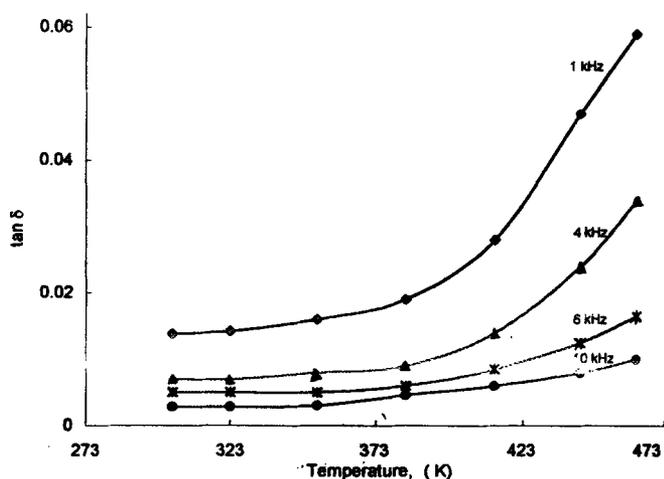
It is interesting to find that the nature of variation of

ε and tan δ with temperature for these glasses is similar. The variation of ε with temperature can be connected to frequency through modified Debye equation as reported earlier (Veeraiah 1987). 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 Tb^{3+}-doped glasses (glass D) is shown in figure 9; the graphs are straight lines about the same slope for all the frequencies in high temperature region. The computed activation energy is 0·98 eV. This value is practically the same as the activation energy for a.c. conduction in the same temperature region in these glasses (table 2). 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 three glasses and yielded similar results. Further, this activation energy too increases from glass A to D (table 2).

Normally, the a.c. conductivity, of the amorphous material obeys the equation:

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

with $s < 1$ 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 $LiF-B_2O_3$: Ln^{3+} glasses on the basis of quantum mechanical tunnelling (QMT) model. In general, the defect centres that could contribute to the conductivity are randomly distributed in these glasses. According to QMT model, only those pairs of carriers which are separated by the hopping distance R, given by:

$$R = (1/2\alpha) \ln (v_{ph}/\omega), \tag{3}$$

Figure 5. Variation of dielectric loss tan δ with temperature at different frequencies for glass B.
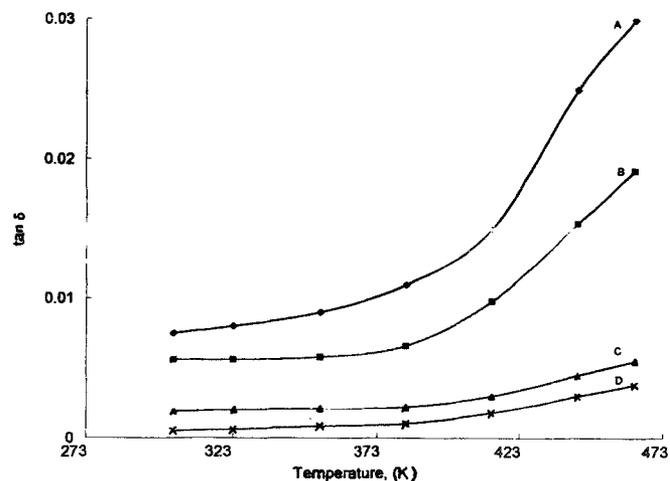

Figure 6. Variation of dielectric loss tan δ with temperature at 5 kHz for all the glasses.

contribute significantly to the conduction. With this, the equation for a.c. conductivity due to quantum mechanical tunnelling is given by (Austin and Mott 1969):

$$\sigma(\omega) = \eta e^2 kT/3 \, [N(E_F)]^2 \, \alpha^{-5}\omega \, [\ln(v_{ph}/\omega)]^4, \qquad (4)$$

where $N(E_F)$ is the density of the energy states near the Fermi level, α the electronic wave function decay constant, v_{ph} the phonon frequency and η a constant and its value is given as $\eta = \pi/3$ (Austin and Mott 1969),

Figure 7. Variation of a.c. conductivity σ with $1/T$ for glass C at different frequencies.
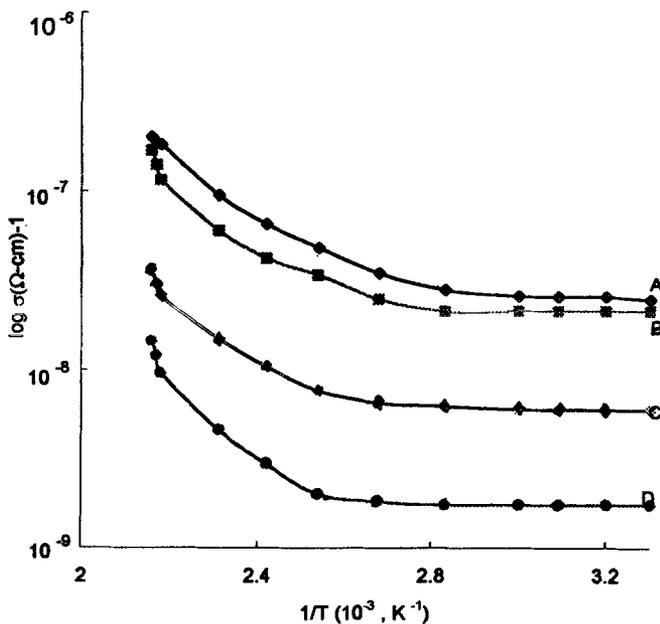
Figure 8. Comparison of variation of conductivity with $1/T$ for all the glasses at 10 kHz.

$= 3.66 \pi^2/6$ (Butcher and Hyder 1977), $= \pi^4/96$ (Pollak 1971).

The frequency exponent s is defined as:

$$s = \partial(\ln \sigma)/\partial(\ln \omega). \qquad (5)$$

Substitution of (4) into (5) results in the following:

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

Thus the quantum mechanical tunnelling of a carrier through the potential barrier between the sites separated by a distance R demands that s should be temperature independent. The plots of $\log \sigma(\omega)$ vs $\log \omega$ for Ce³⁺-doped glasses (glass A) at a temperature of 473 K are shown in figure 10. The graph obtained is almost a straight line. Plots drawn for the other glasses have also yielded straight lines. These results indicate that the exponent s is independent of frequency, which is not fully consistent with (6).

Perhaps the more accurate model for a.c. conduction in which s is less dependent (as observed for these glasses) for a.c. conduction in LiF–B₂O₃ : Ln³⁺ glasses is the correlated barrier hopping (CBH) model (Elliott 1987) in which the height of the potential barrier is correlated with inter site separation. According to this model:

$$s = 1 - \{6kT/[E_0 - kT\ln(1/\omega\tau_0)]\}, \qquad (7)$$

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 according to (7) for the same change in the frequency for a fixed optical band gap. Hence (7) can be assumed to provide a more accurate value of s than (6) for the present glasses, and therefore the CBH model can be considered more appropriate than the QMT model for a.c. conduction
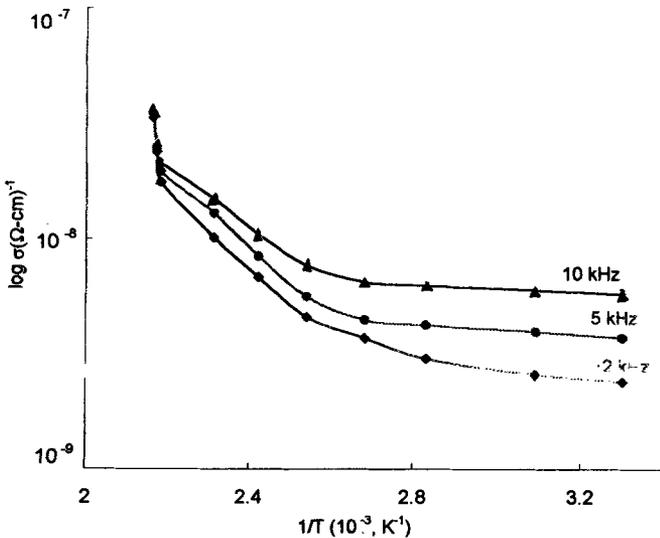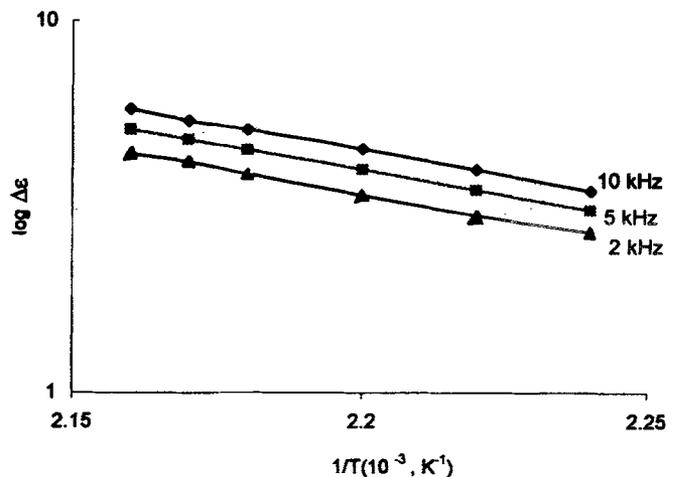

Figure 9. Log $\Delta\varepsilon$ vs $1/T$ at different frequencies for glass D.

in these glasses. However, further analysis on a.c. conduction for these glasses is made 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 the glasses A, B, C and D are presented in table 2.

Considering

$$\sigma \alpha e^{-2\alpha R}, \tag{8}$$

as valid at low frequencies, the value of α is determined by plotting $\log \sigma$ against R (figure 11); here the hopping distance R is evaluated using

$$R = M^{1/3}/(N_A M_i d)^{1/3}. \tag{9}$$

In the above equation, M is the average molecular weight of the glass, d the density, N_A the Avagadro number and M_i the RE^{3+} ion concentration in mole percent. The average value of α obtained from graph 10 is 0.78 Å^{-1}.

Among various mechanisms for conduction in

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 $LiF-B_2O_3 : Ln^{3+}$ glasses in the low temperature region (up to 85°C) 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, at 10^4 Hz and at 353 K, taking α equal to 0.78 Å^{-1} and $q_{ph} \sim 5 \times 10^{12}$ Hz, is calculated using (4), with value of numerical constant η suggested by different investigators and presented in table 2. The value of $N(E_F)$ is found to decrease from glass A to D. Furthermore, the range of $N(E_F)$ values obtained is found to be 10^{20} eV^{-1}/cm^3. Such values of $N(E_F)$ suggest the localized states near the Fermi level (Elliott 1987). The decrease in the conductivity from glass A to D can be due to the decrease in the density of these energy states.

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):

$$\rho_1 = E^2 \omega \varepsilon_0 \varepsilon \tan \delta \text{ W/m}^3. \tag{10}$$

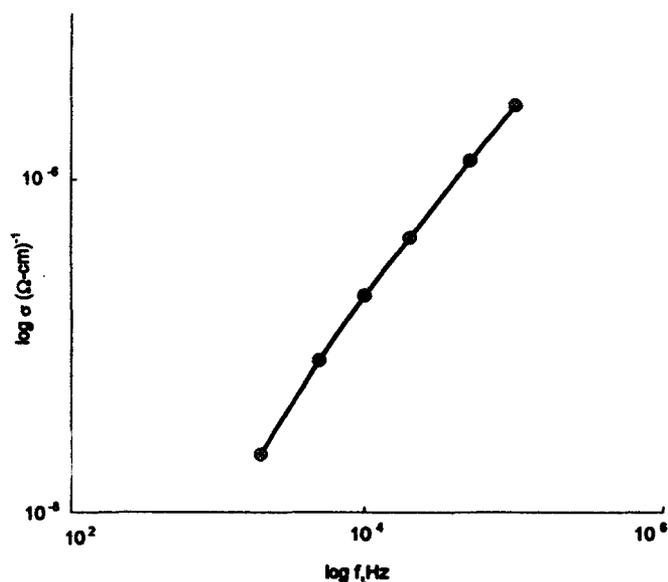This equation indicates that higher the values of

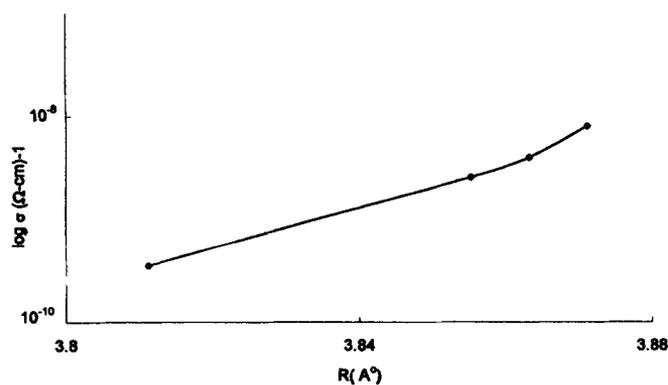**Figure 10.** $\log \sigma(\omega)$ versus $\log \omega$ at 473 K for glass B.

Figure 11. Log σ versus hopping distance R for $LiF-B_2O_3 : Ln^{3+}$ glasses.

Table 2. Data on a.c. conductivity for $LiF-B_2O_3$ glasses.

Glass	$N(E_F)$ in (10^{20} eV^{-1}/cm^3) Austin and Mott	According to Butcher and Hyder	Pollak	S_{exp}	Activation energy (eV) from a.c. conduction	$\Delta \varepsilon$	Dielectric breakdown strength (kV/cm)
A	6·64	5·30	6·75	0·86	0·718	0·72	13·14
B	5·80	4·62	5·89	0·84	0·78	0·79	13·47
C	5·96	4·75	6·06	0·82	0·89	0·90	13·88
D	5·21	4·16	5·30	0·81	0·96	0·98	15·67

$\varepsilon\tan\delta$ of the glass at a given frequency, the higher are the losses. In a dielectric across which the voltage is applied, heat is liberated; followed by a rise in the temperature of the dielectric and further losses occur. The dielectric breakdown strength is inversely proportional to the specific dielectric loss represented by (10).

From the data on breakdown strengths of LiF–B_2O_3 : Ln^{3+} glasses (table 2), the rate of increase of $\varepsilon\tan\delta$ with temperature is highest for Ce^{3+}-doped glass (glass A) and minimum for Tb^{3+}-doped glass (glass D). Though the breakdown strengths are actually determined at room temperature, the heat liberated during the breakdown raises the temperature of the glass and hence raises the $\varepsilon\tan\delta$ value. Since the rate of increase of $\varepsilon\tan\delta$ with temperature is highest for glass A, the breakdown strength is lower when compared with the other glasses. Thus the experiments on the dielectric breakdown strength of LiF–B_2O_3 : Ln^{3+} glasses reveal that there is a decrease in the concentration of defects (such as dangling bonds and point defects) in the glasses with decrease in the ionic radius of the rare-earth dopants.

From the results of various dielectric measurements on LiF–B_2O_3 : Ln^{3+} glasses, it is observed that with a decrease in the ionic radius of the rare-earth dopants, there is a decrease in the rates of increase of ε, $\tan\delta$, σ_{ac} with temperature and increase in the values of activation energy for a.c. conduction and dielectric breakdown strength of these glasses. Thus, there is an increase in the degree of depolymerization of B_2O_3 glass network with increase in the ionic radius of the rare earth dopants.

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