RESEARCH ARTICLE

The influence of Ag$_2$O on the dielectric properties of LiF-CaO-B$_2$O$_3$ glasses

K.SAMBASIVA RAO[*1], N.KRISHNAMOHAN[2]

[1]Department of Physics,J.K.C.College, Guntur,A.P,India
[2]Department of Physics,A.N.R.College, Gudwada,A.P,India
*drksrjkc@gmail.com

Scan QR Code for More details

ABSTRACT

LiF-CaO-B$_2$O$_3$:Ag$_2$O glasses have potential applications in solid state ionic devices, such as solid state batteries, fuel cells, gas sensors, electrochemical capacitors, electro chromic displays, analog memory devices in the far infrared region. Addition of Ag$_2$O to LiF-CaO-B$_2$O$_3$ glass matrix is expected to improve the electrical conductivity dramatically. The objective of the present study is to have a comprehensive understanding over the influence of increasing concentration of Ag$_2$O on a.c. conductivity of LiF-CaO-B$_2$O$_3$ glass system from a systematic study on dielectric constant ε, loss tan δ and a.c. conductivity σ_{ac} over a moderately wide range of frequency and temperature.

1. INTRODUCTION

The study of solid electrolytes is receiving wide attention due to their potential applications in solid state ionic devices, such as solid state batteries, fuel cells, gas sensors, electro chemical capacitors, electro chromic displays, analog memory devices, etc. Of all the available solid electrolytes, silver lithium based solid electrolytes show the highest conductivity at ambient temperature. Among different glass electrolytes systems, LiF-CaO-B$_2$O$_3$:Ag$_2$O glasses are observed to be relatively better conducting materials.

Most of the studies available on LiF-CaO-B$_2$O$_3$ glasses are on the understanding of DC conductivity mechanism [1-4]. Virtually no detailed studies on dielectric properties such as dielectric constant ε, loss tan δ, ac conductivity σ_{ac} over a range of frequency and temperature and breakdown strength of LiF-CaO-B$_2$O$_3$ systems are available. Study on these properties of glasses helps in understanding the conduction mechanism and can also be used as a tool to throw some light on the structural aspects of the glasses [5,6].

In this work, an attempt is made to understand the influence of Ag$_2$O on ac conduction of LiF-CaO-B$_2$O$_3$ glass system from a systematic study on dielectric constant ε, loss tan δ and a.c. conductivity σ_{ac} over a moderately wide range of frequency and temperature.

2. Experimental

The glasses used for the present study are prepared by the melting and quenching techniques [1-3]. Batch materials to produce 10 g of each glass were accurately weighed, thoroughly mixed in an agate mortar and melted in a platinum crucible. Appropriate amounts (all in mol %) of reagent grades of H_3BO_3, $CaCO_3$, Li2CO3 and Ag_2O powders were thoroughly mixed in an agate mortar and melted in a thick walled platinum crucible in the temperature range 900-950°C .The furnace used was a PID temperature controlled furnace (Fig. 2.1). The glasses were melted in a thick walled platinum crucible for an hour till a bubble free liquid was formed. The resultant melt was poured on a rectangular brass mould (having smooth polished inner surface) held at room temperature and subsequently annealed at 200° C in another furnace. The weight of the glass obtained always agreed with that anticipated in the batch, with an error of 0.2 to 0.5 % wt loss in each case. The results indicate that the actual glass compositions are essentially equal to those based on the glass batch. The glasses were then ground and optically polished. The approximate final dimensions of the glasses used for present study are 1 cm x 1 cm x 0.2 cm. For dielectric measurements thin coating of silver paint was applied on either side of the glasses, to serve as electrodes.

With in the glass-forming region of LiF-CaO-B_2O_3 glass system, the following particular compositions with successive increase in the concentration of Ag_2O are chosen for the present study:

A_0: 40 LiF-5 CaO-55 B_2O_3

A_2: 39.8 LiF-5 CaO-55 B_2O_3: 0.2 Ag_2O

A_4: 39.6 LiF-5 CaO-55 B_2O_3: 0.4 Ag_2O

A_6: 39.4 LiF-5 CaO-55 B_2O_3: 0.6 Ag_2O

A_8: 39.2 LiF-5 CaO-55 B_2O_3: 0.8 Ag_2O (all are in mol %)

The density (d) of the glasses was determined by the standard principle of Archimedis' using o-xylene (99.99 % pure) as the buoyant liquid. A direct reading balance (capacity 100 g, readability 0.1 mg) was used for weighing. The bulk glass was suspended on a very thin copper strand was set in the immersion liquid container and weighed in the liquid and air. The optical absorption spectra of the glasses were recorded at room temperature in the spectral wavelength range covering 300–2100 nm with a spectral resolution of 0.1 nm using JASCO Model V-670 UV–vis–NIR spectrophotometer. Infrared transmission spectra were recorded on a with a resolution of 0.1 cm^{-1} in the spectral range 400–2000 cm^{-1} using potassium bromide pellets (300 mg) containing pulverized sample (1.5 mg). These pellets were pressed in a vacuum die at ~680MPa. The spectra were recorded on Jasco-FT/IR-5300 spectrophotometer.

3. Results

3.1 Physical Parameters

From the measured values of density d and calculated average molecular weight $\overline{M}$, various physical parameters such as silver ion concentration N_i, mean silver ion separation R_i, which are useful for understanding the physical properties of these glasses are evaluated [7] and presented in Table .3.1

Table 3.1: Various physical properties of LiF-CaO-B_2O_3:Ag_2O glasses

Glass	Density (g/cm^3)	Avg. molecular weight $\overline{M}$	Conc. Ag ions. N_i x 10^{22}	Ag ion separation R_i(A$^\circ$)
A_0	2.22	51.63	.....	....
A_2	2.23	52.05	0.51	5.78
A_4	2.24	52.46	1.02	4.60
A_6	2.25	52.87	1.53	4.02
A_8	2.26	53.28	2.04	3.66

3.2.2 Dielectric Properties

The dielectric constant ε' and loss tanδ at room temperature ($\approx$ 30 ^{O}C) and at 100 kHz of pure LiF-CaO-B_2O_3 glasses are measured to be 4.53 and 0.0031 respectively. With the introduction of Ag_2O these

K.SAMBASIVA RAO, N.KRISHNAMOHAN

parameters are found to increase. Further both the values ε' and loss $\tan\delta$ are observed to increase with the decrease in frequency for all the glasses. Fig.3.1 represents the variation of dielectric constant (for different concentrations of Ag_2O) with frequency measured at room temperature. Fig.3.2 shows the variation of the dielectric constant with the concentration of Ag_2O measured at 10 kHz; the value of ε' is observed to increase gradually with an increase in the concentration of Ag_2O. The dielectric loss, $\tan\delta$, at room temperature with the concentration of Ag_2O has exhibited a similar behaviour (Figs. 3.3 & 3.4)

The temperature dependence of ε' at different frequencies for glass A_8 (glass containing 0.8 mol % of Ag_2O) is shown in Fig.3.5 and for different concentrations of Ag_2O at 1 kHz is presented in Fig. 3.6. The dielectric constant ε' is found to increase with temperatures slowly up to about 100 ^{o}C; beyond this temperature it increases rapidly especially at lower frequencies.

The variation of dielectric loss $\tan \delta$ of $LiF-CaO-B_2O_3$ glasses containing 0.2 mol % of Ag_2O (A_2) with temperature at different frequencies is shown in Fig. 3.7. The comparison
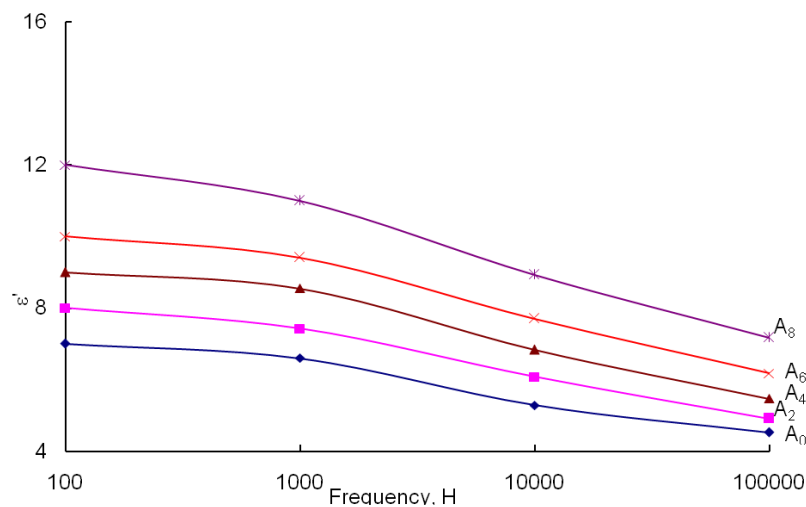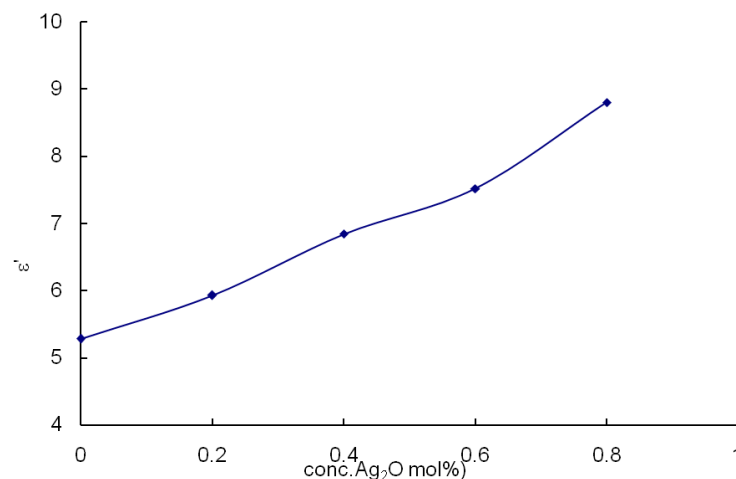

Fig 3.1 The variation of dielectric constant with the frequency of $LiF-CaO-B_2O_3$ glasses containing   different concentrations of Ag_2O measured at room temperature

Fig 3.2   The variation of dielectric constant with the frequency of $LiF-CaO-B_2O_3$ glasses containing   different concentrations of Ag_2O measured at room temperature
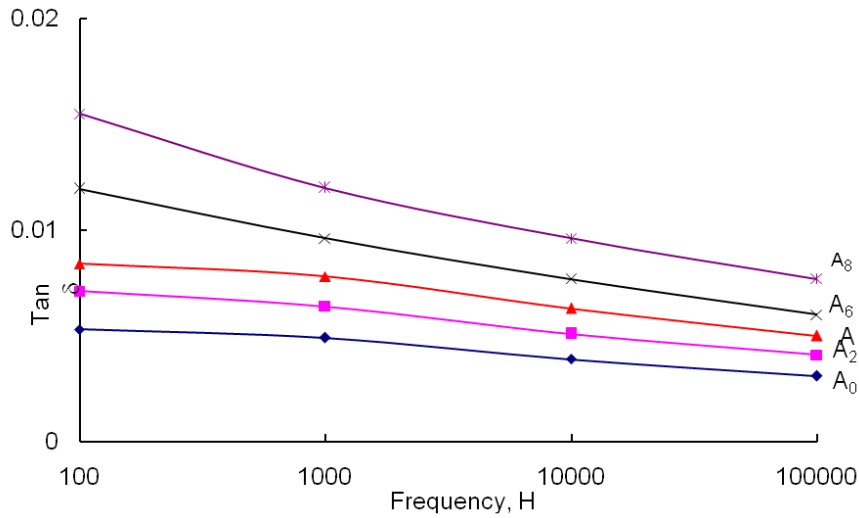
Fig 3.3 The variation of dielectric loss with the frequency of LiF-CaO-B_2O_3 glasses containing different concentrations of Ag_2O measured at room temperature.
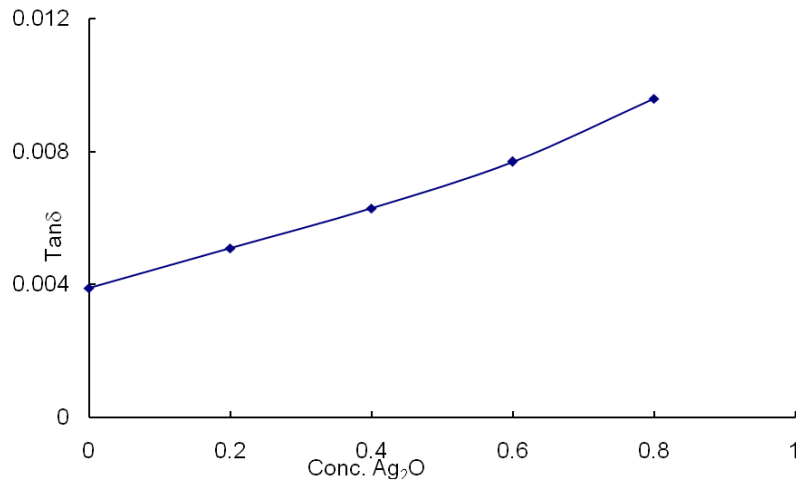

Fig 3.4   Shows the variation of dielectic loss with the concentration of Ag_2O at 10 kHz measured at room temperature
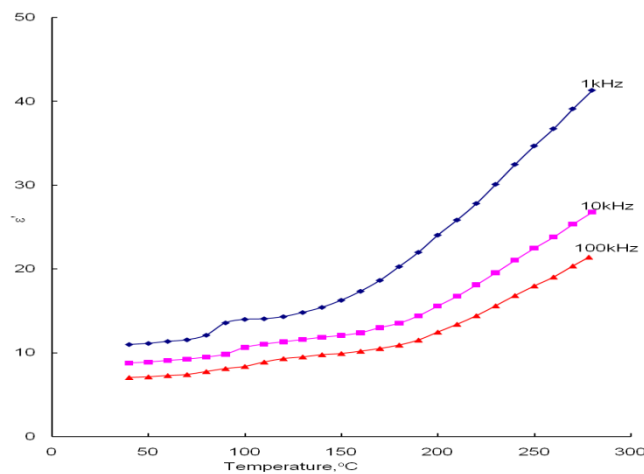

Fig 3.5 Variation of dielectric constant with temperature at different Frequencies for LiF-Cao-B_2O_3 glass containing 0.8 mol % of Ag_2O
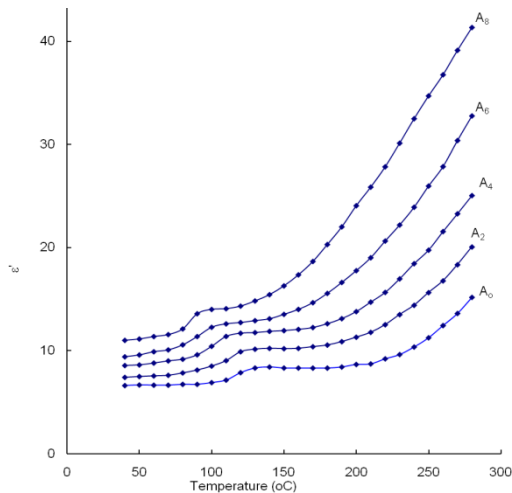
Fig 3.6 Comparision plot of variation of dielectric constant at 1 kHz with temperature for LiF-CaO-B_2O_3 glasses containing different concentrations of Ag_2O
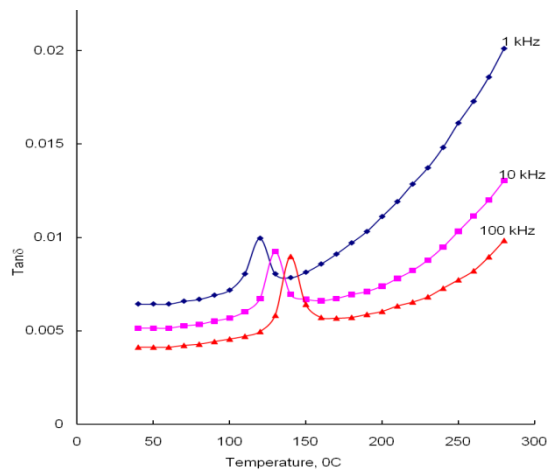

Fig 3.7 Variation of dielectric loss with temperature at different frequencies for LiF-CaO-B_2O_3 glasses containing 0.2 mol % of Ag_2O

plot of dielectric loss variation with temperature for the glasses containing different concentrations of Ag_2O is similar to that for dielectric constant (Fig. 3.8). It is observed that the variation of ϵ' and tan δ (at any fixed temperature and frequency) with the concentration of Ag_2O is similar to that at room temperature. Further, the loss curves (of pure and Ag_2O doped glasses) have exhibited distinct maxima; with increasing frequency the temperature maximum shifts towards higher temperature and with increasing temperature, the frequency maximum shifts towards higher frequency, indicating the relaxation character of dielectric losses of LiF-CaO-B_2O_3: Ag_2O glasses. The observations on dielectric loss variation with temperature for different concentrations of Ag_2O further indicate a gradual increase in the broadness and (tan δ)$_{max}$ of relaxation curves with increase in the concentration of Ag_2O.
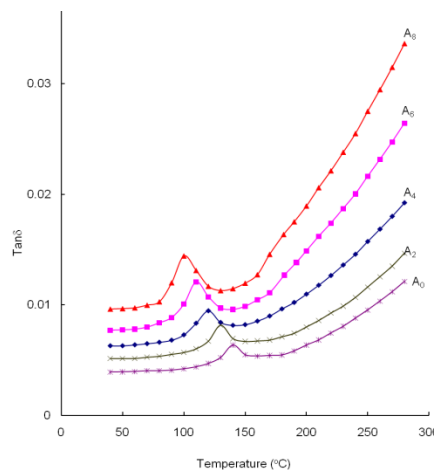
Fig 3.8 A comparison plot of variation of dielectric loss with temperature measured at 10 kHz for LiF-CaO-B_2O_3-Ag_2O glasses

Using the relation:

$$f = f_O \exp(-W_d/KT) \tag{3.1}$$

the effective activation energy, W_d, for the dipoles is calculated; the value of activation energy for the pure glass is estimated to be 2.86 and found to decrease gradually with the increase in the concentration of Ag_2O (Table 3.2).

K.SAMBASIVA RAO, N.KRISHNAMOHAN

Table 3.2: Data on dielectric loss of LiF-CaO-B_2O_3:Ag_2O glasses

Concentration of Ag_2O (7mol %)	$(Tan\delta)_{max}$ at10 kHz	Activation energy for dipoles (eV)
0	0.0058	2.86
0.2	0.0076	2.07
0.4	0.0092	1.76
0.6	0.011	1.27
0.8	0.013	1.05

The a.c. conductivity σ_{ac} is calculated at different temperatures using the equation:

$$\sigma_{ac} = \omega\, \varepsilon'\, \varepsilon_o \tan\delta \,, \qquad\qquad (3.2)$$

(where ε_o is the vacuum dielectric constant) for different frequencies and the plots of log σ_{ac} against 1/T are shown in Fig.3.9 for glass A_4 at different frequencies. The variation of σ_{ac} with 1/T for the glasses doped with different concentrations of Ag_2O measured at 100 kHz is shown in Fig.3.10. From these plots, the activation energy for conduction in the high temperature region over which a near linear dependence of log σ_{ac} with 1/T could be observed, is evaluated and presented in Table 3.3; the activation energy is found to decrease with increase in the concentration of Ag_2O.
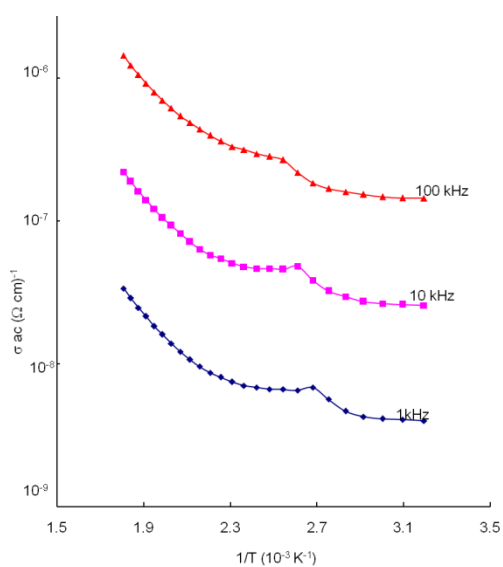

Fig 3.9 Variation of s_{ac} with 1/T for LiF-CaO-B_2O_3 glasses containing 0.6 mol% of Ag_2O
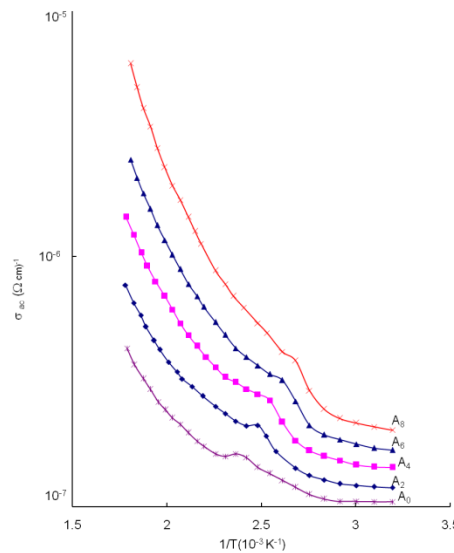
Fig 3.10 Variation of s_{ac} with 1/T for LiF-CaO-B_2O_3 glasses doped with different concentrations of Ag_2O at 100 kHz

Table 3.3 Summary of data on a.c conductivity of LiF-CaO-B_2O_3:Ag_2O glasses

Sample	$N(E_F)$ in (10^{21}, 1/eVcm^3)			A.E for conduction (eV)
	Austin and Mott	Butcher and Hyden	Pollak	
A0	…..	….	……	0.56
A2	1.65	0.69	1.67	0.49
A4	2.25	0.94	2.29	0.46
A6	2.92	1.22	2.97	0.4
A8	4.43	1.84	4.5	0.38

K.SAMBASIVA RAO, N.KRISHNAMOHAN

3.3. Discussion

It is well known that the B_2O_3 glasses network consists of sp^2 planar BO_3 units and more stable sp^3 tetrahedral BO_4 units. The presence of such units in the borate glasses was proved earlier from the IR spectral studies. The BO_4 unit in the glass network linked to two such other units and one oxygen from each unit with a metal ion and the structure leads to the formation of long chain tetrahedron;

. Earlier NMR investigations by different researchers [8, 9] on alkali fluoro borate glasses indicate that in addition to BO_4 units there exist B (O, F) $_4$ or (BO_3 F) and (BO_2F_2) units in this type of systems; the probable linkages between various ions in the present glasses are shown in Fig.3.11; it is to be noted in the figure that different borate groups are connected by oxygen and that the Li^+ ion located near the fluorine serve as charge compensator.
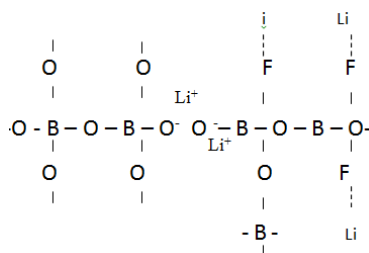

Fig. 3.11. A Schematic illustration of lithium fluoro borate glass

The silver oxide acts as a modifier (normally the oxygens Ag_2O break the local symmetry while Ag^+ ions occupy interstitial positions) and introduces co-ordinated defects known as dangling bonds along with non bridging oxygen ions.

The dielectric constant of a material is due to electronic, dipolar and space charged polarization. All these are active at low frequencies. Infact the nature of variations of ε' with frequency indicate which type of contributions are present. The space charge contribution will depend on the purity and perfection of the glasses. Its influence in general is negligible at very low temperature and noticeable in the low frequency region. The dipolar orientation can sometimes be seen in the glasses even upto 10^6 Hz. Recollecting the data, the slight increase in the dielectric loss at room temperature, particularly at low frequencies for pure and Ag_2O doped – $LiF-CaO-B_2O_3$ glasses may be ascribed to defects produced in the glass lattice which contribute to the space charge polarization.

The temperature has complicated influence on the dielectric constant. Generally increase in the temperature of glasses decrease the electronic polarization. The increase of ionic distance is due to the increase in temperature; influence the ionic and electronic polarization. The decrease in the electronic dielectric constant for many solids is found to be less than 3 % for a temperature changes of about 400^oC [10]. Similarly it appears that the changes in the ionic polarization are not large. Even the presence of dipoles and their contribution to dielectric constant we know from Debye`s theory ε is inversely proportional to temperature. As such it is expected that dielectric constant of Ag_2O doped $LiF-CaO-B_2O_3$ glasses should not change considerably with temperature. However, we find a large increase of ε' and $\tan\delta$ (beyond relaxation region); such a behaviour can only be attributed to the space charge polarization due to bonding defects of the type mentioned earlier in the glasses [11-14]. The change in ε' and $\tan\delta$ with temperature are smaller at higher frequencies as this type of polarization decreases appreciably with frequency.

Variation of ε' and $\tan\delta$ with temperature is observed to be maximum for the glasses containing higher concentration of Ag_2O. This indicates that an increase in the lattice distortion in $LiF-CaO-B_2O_3$ glasses with increase in Ag_2O concentration thus resulting in the enhancement of the space charge polarization, which ultimately causes larger increase of ε' and $\tan\delta$ values as observed in the present measurements. Obviously this is due to increasing modifying action of silver ions similar to lithium ions.. As modifiers these oxides enter the glass network by breaking up B-O-B bonds and introduces dangling bonds. The bonding defects thus

produced create easy pathways for the migration of charges that would build up space charge polarization leading to the increase in the dielectric parameters of the glasses.

The observed dielectric relaxation effects may be attributed due to association of Ca^{2+} ions with a pair of cationic vacancies (which exhibit the vibrational bands in the high frequency side of P=O vibrational region) in analogy with the mechanism-association of divalent positive ion with a pair of cationic vacancies – in conventional glasses, glass ceramics and crystals[15,16]. The increasing values of $(tan\delta)_{max}$ and decreasing value of the effective activation energy associated with the dipoles for the glasses A_0 to A_8 obviously suggests an increasing freedom for dipoles to orient in the field direction due to increasing degree of disorder in glass network, vividly, due to the increasing the modifying action of Ag^+ ions.

The high temperature part of a.c conductivity can be explained on the basis of ionic conduction as presented below. Fig 3.12 & 3.13 show that the a.c conductivity increases with increase of Ag_2O content in the glass system. Further, the activation energy for conduction decreases with increase of Ag_2O content in these glasses and is found to be the lowest for the highest conducting glass. This is obviously because of the increase in mobility and the concentration of charge carriers (Ag^+) that contribute to the conduction, with increase in Ag_2O content in the glasses. The relation between conductivity and the concentration of charge carriers, is given by $\sigma = ne\mu$, where n is number of charge carriers, e is charge and μ is mobility. This relation suggests that the increase in the concentration of silver ions may enhance the conductivity. This clearly suggests the increase in the conductivity with the temperature is mainly due to an increase in the mobility of ions [17]. The range of activation energies obtained for these glasses also suggests that there is an every possibility for the Li^+ ions also to participate in the conduction in the high temperature region [18].

The low temperature part of the conductivity (a near temperature independent part, as in the case of present glasses upto nearly 553 K) can be explained on the basis of quantum mechanical tunnelling model [19].

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:

$$\sigma(\omega) = A\omega^s, \tag{3.3}$$

With the exponent s < 1 (up to the frequency of 1 MHz), is considered to signify the coupling of an ion's movement with its environment [20].
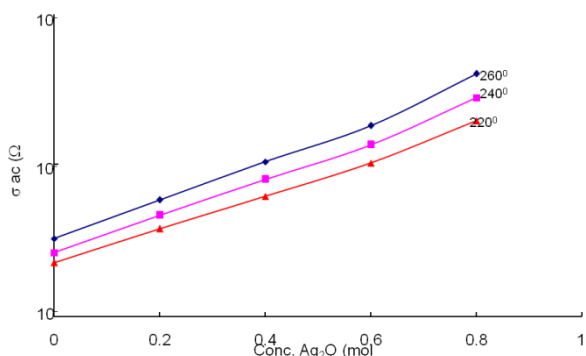

Fig 3.12 Isotherms of ac. Conductivity (100 kHz) of LiF-CaO-B_2O_3 glasses with the concentration of Ag_2
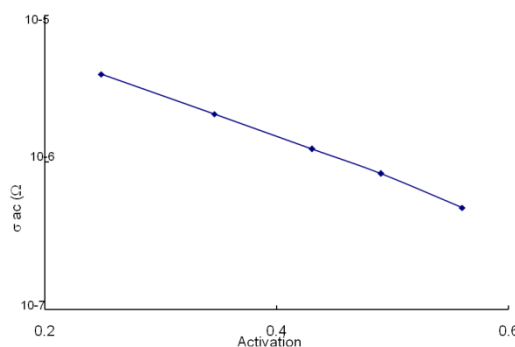
Fig 3.13 Variation a.c condductivity with the activation energy of LiF-CaO-B_2O_3-Ag_2O glasses

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

$$R_\omega = (1/2\alpha)\ \ln(\nu_{ph}/\omega) \tag{3.4}$$

contribute significantly to the conduction. With this, the equation for a.c. conductivity due to quantum mechanical tunnelling is given by [21]:

$$\sigma(\omega) = \eta e^2 KT\ [\ N(E_F)\ ]^2\ \alpha^{-5}\omega\ [\ \ln(\nu_{ph}/\omega)\ ]^4, \tag{3.5}$$

K.SAMBASIVA RAO, N.KRISHNAMOHAN

where N (E_F) is the density of the energy states near the Fermi level, α is the electronic wave function decay constant, ν_{ph} is the phonon frequency and η is a constant and its value is given by $\eta = \pi/3$ (Austin & Mott [20]), $= 3.66\pi^2/6$ (Butcher & Hyden [22]), $= \pi^4/96$ (Pollak [23]).

The frequency component s is defined as:

$$s = \frac{\partial(\ell n \sigma)}{\partial(\ell n \omega)} \quad . \tag{3.6}$$

Substitution of (3.6) into (3.7) results :

$$s = 1 - \frac{4}{\ln(1/\omega\tau_o)} . \tag{3.7}$$

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 but dependent on frequency. The plot of log $\sigma(\omega)$ *vs.* log ω for glass A_6 at temperature 353 K is shown in Fig. 3.13 . Plots drawn for other glasses have also yielded straight lines. These results indicates that the exponent s is independent of frequency, which is not fully consistent with equation (3.7) . Possibly, the more appropriate model is the atomic hoping model for an a.c conduction in which s is less dependent on frequency as observed for the present LiF-CaO-B_2O_3: Ag_2O glasses.

Among various mechanisms of conduction in the amorphous materials (such as band conduction, conduction in extended states, conduction in localized states near the band edge and conduction in the localized states near the Fermi level), the conduction in the localized states near Fermi level occurs when a.c. conductivity is nearly temperature independent and varies linearly with frequency. The conduction in the present LiF-CaO-B_2O_3: Ag_2O glasses in the low temperature region (up to 373 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 10^5 Hz at T=343 K, taking $\alpha = 0.50$ (Å)$^{-1}$ (obtained by plotting log σ_{ac} against R_i) and $\nu_{ph} \sim 5 \times 10^{12}$ Hz, is computed using equation (3.5), with the value of numerical constant η suggested by different investigators and presented in Table 3.3 The value of N(E_F) is found to increase from A_0 to A_8. Furthermore, the range of N(E_F) values obtained $\approx 10^{20}$ eV^{-1} cm^{-3} ; such values of N[E_F] suggest the localized states near the Fermi level.

Conclusions

1. The dielectric constant ε, at room temperature (30 ^{o}C) and at 100 kHz of pure LiF-CaO-B_2O_3 glasses is measured to be 4.53 and the value is found to increase with the decrease in frequency. The dielectric loss at room temperature for pure glasses exhibited similar behavior.

2. With the introduction of Ag_2O in to LiF-CaO-B_2O_3 glass matrices, the values of dielectric constant and loss are found to increase with increase in the concentration of Ag_2O.

3. The variation of dielectric constant of LiF-CaO-B_2O_3: Ag_2O glasses with temperature shows a considerable increase especially at lower frequencies ; such behavior has been attributed to the space charge polarization due to bonding defects created by silver and lithium ions.

4. The variation of dielectric loss of pure and Ag_2O doped LiF-CaO-B_2O_3 glasses has exhibited dielectric relaxation effects. With increase in the concentration of Ag_2O, the dielectric relaxation intensity has been observed to increase whereas the activation energy for the dipoles has been observed to decrease. From these observations, it has been concluded that there is an increasing degree of disorder (or the increasing freedom for dipoles to orient in the field direction) with the increase in the concentration of Ag_2O. The relaxation effects have been attributed due to association of Ca^{2+} ions with a pair of cationic vacancies

5. The ac conductivity σ for Ag_2O doped glasses has been found to increase with the increase in the concentration of Ag_2O. The activation energy for ac conduction is found to decrease with increase in the concentration of Ag_2O. The ac conductivity of these glasses found to obey the relation $\sigma(\omega)=A\omega^s$;

low temperature part of ac conductivity phenomenon has been explained on the basis of quantum mechanical tunneling of electrons. The density of the defect energy states $N(E_F)$ near the Fermi level for these glasses has been calculated. The range of the values of $N(E_F)$ obtained suggests that the ac conduction is due to the localized states is near the Fermi level. The value of $N(E_F)$ is found to decrease with increase in the concentration of Ag_2O.

6. The conduction in the high temperature range could successfully be explained on the basis of ion conduction.

Summing up the entire work presented in this paper it is felt that when Ag_2O is increased in the LiF-CaO-B_2O_3 glass network silver ions mostly take modifying positions create easy path ways for the migration of charge carriers and also contribute to the conductivity.

References

[1]. D.Dutta andA.Ghosh,J.phys,: Condens.Matter 16(2004)2617
[2]. M.M angion and G.P. Johari,phys.Rev.B36(1987)8845
[3]. O.Sipr,G.Dalba,F.Rocca,phys.chem.Glasses 44 (2003) 252-5.
[4]. N.Satyanarayana,A.arthikeyan,M.Venkateswarlu,B.Rambabu.42 (2001) 67.
[5]. P.Subbalakshmi,N.Veeraiah,J.Non-Cryst.Solids 298 (2002) 89.
[6]. D.K.Durga,N.Veeraiah,J.Matter.Sci.36 (2001) 5625.
[7]. M.M.Ahmed,C.A.Hogarth,M.N.Khan, J.Matter.Sci. 19(1984) 4041.
[8]. C.H.R. Jager, U. Haubeneisser, Phys. Chem.. Glasses, 26 (1985) 152.
[9]. K.D. Line, P.J. Bray, Phys. Chem.. Glasses, 7 (1966) 41.
[10]. V.Ravikumar,N.Veeraiah,Phys.Stat.Solidi 147(1995) 601.
[11]. P.Subbalakshmi,P.S.Sastry, N.Veeraiah, ,phys.chem.Glasses 42 (2001) 307.
[12]. P. Subbalakshmi, N.Veeraiah, J.Non-cryst. solids 298 (2002) 89.
[13]. D.K.Durga,N.Veeraiah,J.Matter.Sci.36 (2001) 5625.
[14]. G. Srinivasa Rao, N.Veeraiah, J. Solid State.Chem.166 (2002) 104
[15]. D.K. Durga, N. Veeraiah, J. Mat. Sci. 36 (2001) 5625.
[16]. S. Radha Krishnan, R.S. Srinivas, Phys. Rev. B 14 (1976) 6967.
[17]. G.El-Damrawi, Phys. Stat. Solidi (a) 177 (2000) 385.
[18]. N.Veeraiah. J.Mater.Science 22 (1987) 2017
[19]. K.L. Nagai., Comments Solid State Phys. 9 (1979) 127;9 (1980) 41.
[20]. I.G. Austin And N.F. Mott, Adv. Phys.18 (1969) 657.
[21]. S. R. Elliot, "Physics of amorpous materials", (Longman, Essex 1990).
[22]. P.Butcher And K.J. Hyden, Phil. Mag.36 (1997) 657.
[23]. M. Pollak, Phil. Mag.23 (1971)579.