Spectroscopic and transport studies of Cu^{2+} ion doped in $(40 - x)Li_2O$–$xLiF$–$60Bi_2O_3$ glasses

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Abstract. The preparation of $(40 - x)Li_2O$–$xLiF$–$60Bi_2O_3$ glassy system and spectroscopic and transport studies of this system are reported. IR results show that this glass consists of $[BiO_3]$ units and indicate formation of Bi–F bonds with the addition of LiF. From the ESR spectra of Cu^{2+} ion, the effective g values are found to vary slightly with increasing concentration of fluorine ion. The optical absorption peak corresponding to Cu^{2+} increased linearly with increasing concentration of LiF between 620 nm and 728 nm except at 2·5 mole% of LiF where its value is 729 nm. This peculiar behaviour is attributed to the varying structural coordination of fluorine as the concentration of lithium fluoride is increased. The ionic conductivity measurements indicate that the conduction is due to adiabatic hopping of polarons and the activation energies are found to be temperature and concentration dependent.

Keywords. Preparation; $(40 - x)Li_2O$–$xLiF$–$60Bi_2O_3$ glasses; spectroscopic and transport studies.

1. Introduction

The need to develop efficient electrochromic cells and solid state batteries has led to investigation of the various amorphous materials. Since the conductivity of glasses is many orders greater than its crystalline counterparts and together with the absence of grain boundaries, made glasses as most useful materials in industry (Ingram 1987). The conductivity of glasses is very high at temperatures considerably lower than their melting point. Fast ionic conducting glasses are very much important and have a wide range of applications in industry and other allied areas such as battery materials, photochromic cells, electrochromic devices, etc. Glasses that are found to be superionic conductors are of alkali cations Li, Na, K, Ag and Cu with a network-forming oxides like Si_2O, B_2O_3, P_2O_5, etc. Glasses offer larger number of advantages over crystalline electrolytes including physical isotropy, absence of grain boundaries, continuously variable composition, ease of thin film formation for device application and good stability. Lithium based glasses are mostly fast ionic conductors. Irrespective of the radius of the cation the conductivity is very high (Glass and Nassau 1980). The lithium ion conductivity is enhanced by the addition of alkali halogens in the glasses (Ramana *et al* 1992). Bismuth based glasses are very useful because of their high conductivity.

In this paper ESR, optical and transport properties of $(40 - x)Li_2O$–$xLiF$–$60Bi_2O_3$ glasses are presented. The change in the composition of lithium fluoride in the base glass influences their structure and the transport properties. The structure of the glass is discussed on the basis of spectroscopic studies. The conductivity mechanism is discussed on the basis of small polaron hopping model.

2. Experimental

The starting chemicals lithium carbonate, lithium fluoride and bismuth oxide were all of analar grade, and were weighed in proper proportion to get 10 g of each glass. The powders were ground thoroughly for proper mixing. The powdered mixtures were melted in porcelain crucibles in a carbide rod furnace for 2 h at 1050–1100°C. The molten liquids were stirred frequently to get homogeneity. The melts were quenched at 100°C by pouring on a stainless steel plate and pressed with another stainless steel disk. 1 mole% of CuO was added as an impurity. The colour of pure samples was light yellowish and turned to green after the addition of CuO. The composition of the glass is given in table 1.

X-ray diffraction patterns of the powdered glass samples were recorded using copper target ($K_a = 1·54$ Å) on Phillips PW 1140 diffractometer at room temperature. Infrared transmittance spectra of the glasses were recorded using Perkin-Elmer FT-IS spectrometer model 1605, in the wave number range 400–4000 cm^{-1} at room temperature. ESR spectra of all glasses were recorded using Brucker model ER 200D, SRC spectrometer operating at X-band (9·8 GHz) using 100 KHz field modulation at room temperature. DPPH was used as the standard g

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(*g* = 2·0037) marker. Optical absorption spectra of the glasses of about 1 mm thickness were recorded with Shimadzu UV-3100 spectrometer in the wavelength range 190–1000 nm, at room temperature taking air as a reference medium. The peak-pick facility provided in the spectrometer was used to measure the peak position. D.c. conductivity measurements of pure and copper doped glasses of 2 mm thickness were carried out using home built conductivity zig and Keithley 616 type electrometer.

3. Results

3.1 *XRD and IR spectra*

The X-ray diffraction spectra of all glass samples show no peaks confirming the amorphous nature of the samples. The infrared transmittance spectra of the glass samples (G_1, G_2, G_3 and G_5) are shown in figure 1 which is recorded as a function of wave number versus percentage of transmittance. From the IR spectrum it is observed that for G1 (fluorine free) glass a peak is observed at 890 cm^{-1}. At $x = 2·5$ mole% of LiF (G2 glass) this peak is observed at 926 cm^{-1} and for G3 and G5 glasses it is observed at 910 cm^{-1}. Therefore, IR spectra suggests that the glass composition consists of BiO_3 pyramidal units and fluorine enters into the network structure of the glass (Sreenivasu and Chandramouli 2000).

3.2 *Optical absorption spectra*

Optical absorption spectra for all the glass compositions exhibit a single broad peak in the range 690–729 nm, which can be attributed to the presence of Cu^{2+} ion in the glass. This absorption can be assigned to the $^2E_g \rightarrow {}^2T_{2g}$ transition of Cu^{2+} ion (Sakka *et al* 1978; Ohishi *et al* 1983).

The absorption peak wavelengths at different concentrations of LiF are given in table 2. The absorption peak of Cu^{2+} is shifted towards higher wavelength with increasing concentration of lithium fluoride. The peak corresponding to Cu^{2+} goes through a maximum at $x = 2·5$ mole% of LiF. As the fluorine ions replace the oxygen ions of the metal ion, the field around probe ion decreases with increasing concentration of fluorine (Sands 1955; Ramana *et al* 1992). As the ligand field produced by the array of fluorine ions is less than that of the oxy-

gens the peak shifts towards higher wavelength with increasing fluorine ion concentration. The departure of peak value at $x = 2·5$ mole% of LiF is due to varying structural coordination of fluorine as a function of its concentration and this result is further discussed later.

3.3 *ESR spectra of Cu^{2+} ion*

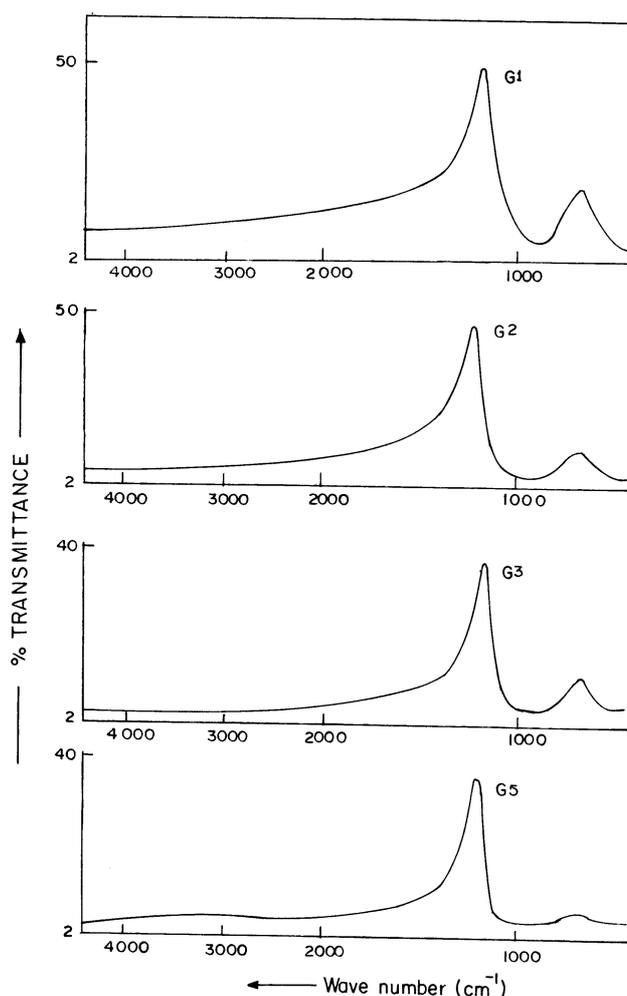The ESR spectra of all the samples gave only broad resonance lines, the hyperfine splittings are not resolved in

Figure 1. IR spectra of $(40 - x)Li_2O–xLiF–60Bi_2O_3$ glass system.

Table 1. Composition of $(40 - x)Li_2O–xLiF–60Bi_2O_3$ glass system.

Sample	Composition (mole%)
G1	$40Li_2O–60Bi_2O_3$
G2	$37·5Li_2O–2·5LiF–60Bi_2O_3$
G3	$35Li_2O–5LiF–60Bi_2O_3$
G4	$32·5Li_2O–7·5LiF–60Bi_2O_3$
G5	$30Li_2O–10LiF–60Bi_2O_3$

Table 2. Absorption peak of Cu^{2+}, g_{eff} and ΔH_{pp} values of $(40 - x)Li_2O–xLiF–60Bi_2O_3$ glass system.

Sample	Cu^{2+} peak (nm)	g_{eff} ($\pm 0·002$)	ΔH_{pp} (G)
G1	690	2·096	220
G2	729	2·092	225
G3	712	2·097	210
G4	718	2·101	230
G5	728	2·103	230

the spectrum. The effective *g* values estimated from the observed ESR spectra are given in table 2. The peak to peak field width (ΔH_{pp}) is estimated. The absence of hyperfine splittings may be due to the inhomogeneous broadening (Ahmed 1983). The observed effective *g* values (g_{eff}) are increasing monotonically with the concentration of fluorine ion except at $x = 2\cdot5$ mole% of LiF, where it is found to go through a minimum.

The increase in the effective *g* (g_{eff}) values may be attributed to the variation of field around the copper ion as the fluorine ions replace the oxygen ions. Ramana *et al* (1991, 1992) observed similar change in lithium halo borate glasses doped with Cu^{2+} when the concentration of lithium fluoride in the glass is varied. The observed minimum in the variation of g_{eff} value with LiF concentration at $2\cdot5$ mole% is due to varying structural coordination of the fluorine ion. The fluorine ion which takes part in the glass network may replace either the probe ion (Cu^{2+}) oxygen or one of the oxygens of the bismuth which coordinate with the probe ion. Up to $2\cdot5$ mole% of LiF probe ion oxygen may be replaced more easily by fluorine whereas at higher concentrations the oxygens of bismuth coordinating with probe ion are also replaced. IR results also indicate the formation of Bi–F bonds.

3.4 D.c. electrical conductivity

The d.c. conductivity of all the samples is measured in the temperature range 323–523 K, for different compositions of lithium fluoride. Figure 2 shows the conductivity plots of log *s* versus $1000/T$ and reveals nonlinear behaviour, clearly indicating that the conduction mechanism is due to hopping of charge carriers (Ghosh and Chakravorty 1990).
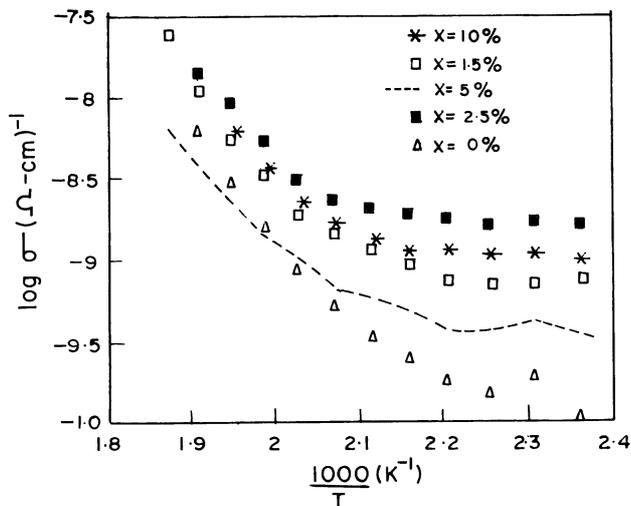

Figure 2. Temperature dependence of d.c. electrical conductivity for $(40 - x)Li_2O-xLiF-60Bi_2O_3$ glass system.

The d.c. conductivity of semiconducting oxide glasses arising from the hopping of polarons in a non-adiabatic approximation is given by (Mott 1968; Yawale and Pakade 1993)

$$s = ne\boldsymbol{m} = \boldsymbol{n}_0 N e^2 R^2/kT\, C(1 - C)\exp(- 2\boldsymbol{a}R)\exp(- W/kT),$$
(1)

where *n* is the number of transport ions and $\boldsymbol{m}$ the mobility, *N* the number of metal ion sites per unit volume, *C* the ratio of ion concentration in low valence state to total concentration of metal ions; the term $\exp(- \boldsymbol{a}R)$ represents the electron overlap integral between sites, *R* the hopping distance and *W* the activation energy.

The calculated activation energies at different temperatures for the varying glass compositions are given in table 3. As can be seen, the activation energies are concentration and temperature dependent. The nonlinear nature of the conductivity indicates that the conduction is electronic in nature (Sayer and Mansingh 1972).

To know whether the hopping mechanism is adiabatic or non-adiabatic in nature the method suggested by Sayer and Mansingh (1972) and Murawski *et al* (1979) is followed. When the overlap integral between sites $J_0 \exp(- \boldsymbol{a}R)$ approaches J_0, i.e. $\exp(- \boldsymbol{a}R) \to 1$, the hopping is adiabatic and it is mainly controlled by the activation energy. The d.c. conductivity is then given by

$$s = \boldsymbol{n}_0 N e^2 R^2/kT\, C(1 - C)\exp(- W/kT).$$
(2)

The plot of activation energy versus composition (mole% of LiF) at different temperatures indicates that with the increase of LiF concentration the activation energy of electrical conduction decreases linearly. The departure of activation energy from original tendency is due to the highly correlated concentration dependence of these properties of the amount of fluorine. Figure 3 shows the plot of log *s* versus activation energy at any selected temperature (455 K) for different compositions of LiF and showed straight-line nature. The temperature estimated from the slope ($1/kT$) is found to be nearly equal to the chosen temperature. The above result indicates that the conduction is due to adiabatic hopping and that it is mainly controlled by the activation energy.

Table 3. Activation energies of $(40 - x)Li_2O-xLiF-60Bi_2O_3$ glass system at different temperatures.

Glass	Activation energy (eV)			
	434·7 K	454·5 K	476 K	500 K
G1	0·840	0·875	0·888	0·885
G2	0·756	0·786	0·815	0·822
G3	0·813	0·850	0·871	0·878
G4	0·787	0·821	0·837	0·845
G5	0·772	0·807	0·831	0·836

4. Discussion

The optical and ESR studies of the glasses using Cu^{2+} as paramagnetic probe clearly indicate the effect of fluorine ion. With increasing concentration of LiF, the effective *g* values (g_{eff}) are found to increase but passes through a minimum at about 2·5 mole% LiF, whereas the optical absorption peak of Cu^{2+} ion goes through a maximum. The above results clearly indicate the change in structure of the glass with the addition of LiF.

Bishay and Maghrabi (1969) found that in ternary Bi_2O_3–B_2O_3–Na_2O glass system, the Bi_2O_3 enters mainly as a network modifier in the range 20–25 mole% of ($Bi_2O_3 + Na_2O$). This is accompanied by an increase in the four coordination of boron and in the number of non-bridging oxygen ions in the structure. From 25–37 mole% of ($Bi_2O_3 + Na_2O$) the bismuth ion becomes strongly bonded to three oxygens, although each is still surrounded by a total of six oxygens. The number of [BO_4] groups decreases in this range of composition. Thus, bismuth attains the coordination of 6 with octahedral grouping of oxygen atoms. The addition of alkali ions breaks the structure and the structure changes to [BiO_3] pyramidal units by decreasing its coordination to 3 (Bishay and Maghrabi 1969; Hazra and Ghosh 1995).

Thus, the number of non-bridging oxygen ions increases with the addition of alkali ion. When lithium fluoride is added to the base glass the fluorine replaces the oxygen ions. When fluorine takes part in the network, it may replace one of the oxygen of the glass network with these two possibilities: (i) It may replace the bridging oxygen or (ii) it may replace non-bridging oxygens of bismuth, that is coordinated to probe ion.

If fluorine is replacing the oxygens of the Bi–O bond, in which bismuth is coordinated to the oxygen of probe ion, it may be responsible for the change in local

environment of the probe ion (Cu^{2+}). The IR spectra (pure and fluorine rich glass) clearly indicate the presence of Bi–O bonds in the pure glass (Bishay and Maghrabi 1969; Hazra and Ghosh 1995). The absorption band at 890 cm^{-1} and 540–620 cm^{-1} can be attributed to Bi–O stretching vibrations of [BiO_3] pyramidal units. In the present investigation, the second bond is not recorded due to limitation of apparatus. It can be seen that the addition of LiF to the glass changes the absorption frequency and the absorption is observed at 926·2 cm^{-1} at $x = 2·5$ mole% of LiF and beyond this concentration it is observed at 909 cm^{-1}. This change in IR spectra caused by the addition of fluorine can be considered as an indication of the formation of Bi–F bonds. Thus, the formation of Bi–F bonds by replacing oxygens of bismuth are in turn affecting the local environment of the probe ion which is reflected in the variation of optical absorption peak of Cu^{2+} ion with the addition of lithium fluoride.

With increasing concentration of lithium fluoride, added to Li_2O–Bi_2O_3 glass, the absorption peak shifts towards higher wavelength. As the ligand field generated by array of fluorines is less than that of oxygens the distortion around the metal ion decreases. Therefore, the absorption peak shifts towards longer wavelength. As LiF is added to the base glass, at around 2·5 mole% of LiF, fluorine ions replace bridging oxygen ions of bismuth. Hence, the distortion around copper(II) ion decreases which reflects a maximum increase of absorption wavelength with composition. At this concentration of LiF the observed change in the IR spectrum indicates the formation of Bi–F bond. At $x = 5$ and above mole% of LiF, fluorine ions start replacing the non-bridging oxygen sites of bismuth also. As the copper ion is likely to be in an interstitial position, the replacement of bridging oxygens by fluorine, the decrease in the ligand field around copper is more and when a non-bridging oxygen is replaced by the fluorine the ligand field around copper ion decreases by lesser amount. Above 5 mole% of LiF, more and more number of non-bridging oxygen ions are replaced by fluorine ions which causes the field around copper to decrease and the absorption peak shifts towards higher wavelength. The change in g_{eff} value with the composition of LiF clearly indicates the variation of distortion around copper(II) ion. Thus, the observed maximum at $x = 2·5$ mole%, in the absorption peak position can be accounted for, on the basis of competitive replacement of the different structural oxygens (bridging and non-bridging ones) by fluorine.

An identical variation is also observed in d.c. conductivity studies. The activation energy decreases with increasing content of LiF and passes through a minimum at $x = 2·5$ mole% of LiF. At lower concentrations in $LiBiO_3$ the Li^+ is necessary for the charge neutrality but not in the structure. The conductivity takes place mostly due to hopping of polarons between two different oxidation states of bismuth and thus the ionic contribution due to the
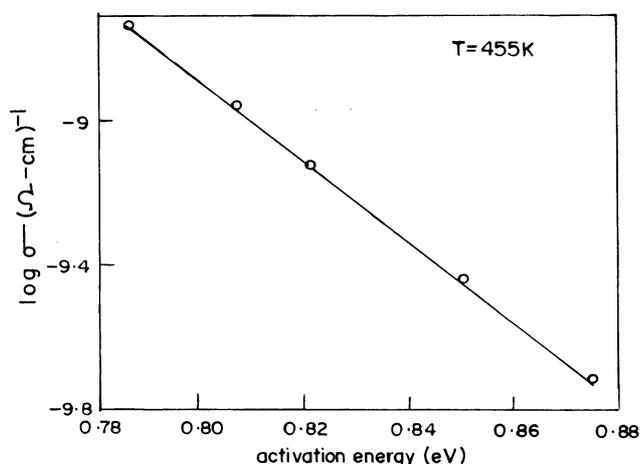

Figure 3. Log *s* versus activation energy at the temperature 455 K for $(40 - x)Li_2O$–$xLiF$–$60Bi_2O_3$ glass system.

mobility of Li ions is less. At $x = 2.5$ mole% of LiF, it may be plausible that the atomic substitutions might have resulted in more vacant interstitial sites which depend partly on the distance over which the concept of charge neutrality can be extended and this may be the reason for conductivity to attain a maximum value. In this composition range the formation of BiO_3 units along with non-bridging oxygen ions create favourable condition for increased conduction. As the fluorine ions are replacing the non-bridging oxygens and one lithium ion is coordinated with one non-bridging fluorine ion for charge neutrality of the structure, the number of mobile ions increases. In addition to polaron hopping the contribution due to mobile lithium ions enhances the conductivity. Therefore, the above results clearly indicate the change in structure of the glass with the addition of LiF.

5. Conclusions

ESR, optical absorption and transport studies reveal that the varying structural coordination of fluorine ion between the ligand oxygen and the non-bridging oxygen coordinating with the bismuth ion might be the reason for the observed results. The conduction mechanism is due to adiabatic hopping of polarons between different valency states of bismuth, and the activation energies are found to be temperature and concentration dependent.

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