EPR, IR and DC conductivity studies of $x\text{CuO}-(100-x)\text{Bi}_2\text{O}_3$ glasses

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Abstract. Glass system $x\text{CuO}-(100-x)\text{Bi}_2\text{O}_3$ in the composition range 30–60 mol% of CuO is prepared by melt-quenching technique. The ESR spectra show no hyperfine splittings in parallel part but the peak to peak field width is found to vary with CuO content. The observed g effective values are found to vary with copper oxide. The absence of hyperfine splittings is due to inhomogeneous broadening. The observed IR spectra suggest the presence of Bi–O bonds. The structure is changing from $[\text{BiO}_6]$ octahedral to $[\text{BiO}_3]$ pyramidal units with increasing CuO concentration. D.C. electrical conductivity results indicate that the conduction is electron in nature and arises out of adiabatic hopping of polarons. The activation energy is found to be concentration and temperature dependent.

Keywords. Preparation of $x\text{CuO}-(100-x)\text{Bi}_2\text{O}_3$ glass system; IR and ESR spectra; d.c. ionic conductivity.

1. Introduction

Transition metal oxides such as CuO, V_2O_5 , etc can form glasses when mixed with glass forming oxides. Electrical conduction in these glasses occurs by the hopping of electrons from an ion of low valency state (Cu^+) to its higher valency state (Cu^{2+}). It has been suggested by Murawski *et al* (1979) that although the thermal activation energy for conduction appears to be the dominating factor which controls the conductivity, in many cases the pre-exponential factor has a great influence on the conductivity. Multi component non-conventional glasses based on Bi_2O_3 are of great interest because they form amorphous materials without any conventional network formers like B_2O_3 , P_2O_5 , etc. Bismuth based glasses are used to produce glass ceramic superconductors (high T_c) with controllable microstructure (Komatsu *et al* 1988; Minami *et al* 1988; Zheng and Meckenzie 1988; Tatsumisago *et al* 1990; Onisi *et al* 1991; Yuan *et al* 1991). Although Bi_2O_3 is not in itself a glass former, because of its highly polarizable nature the coordination number of Bi^{3+} ion may decrease and cations may exist in the glass network in $[\text{BiO}_3]$ pyramids in the presence of conventional glass forming cations. Non-conventional glasses using Bi_2O_3 as the basis of glass network of multi-component systems have been reported (Dumbaugh 1978, 1986). Bismuth based glasses are also used in the fabrication of switching and memory devices. Many glass systems based on Bi_2O_3 have been reported by several authors. Ghosh and Chakraborty (1990) reported d.c. electrical conductivity of semi-

conducting $\text{CuO}-\text{Bi}_2\text{O}_3-\text{P}_2\text{O}_5$ and analyzed that at high temperatures adiabatic hopping theory is most appropriate and at low temperatures variable range hopping mechanism dominates the conduction.

In the present work, the preparation and characterization of $\text{CuO}-\text{Bi}_2\text{O}_3$ glasses by ESR and IR spectral studies are reported. D.c. electrical conductivity studies are carried out for different compositions of these glasses and the conductivity mechanism is discussed on the basis of polaronic hopping model.

2. Experimental

Glass samples were prepared using analar grade CuO and Bi_2O_3 in the composition range $x\text{CuO}-(100-x)\text{Bi}_2\text{O}_3$ where x ranged from 30 to 60 mol%. Appropriate amounts of weighed chemicals were ground in a mortar to produce 10 g each of glass mixture and were melted in an electrical furnace in the temperature range 1323–1473 K depending upon their molar ratio for 2 h. The molten liquid was stirred frequently for homogeneity. The melts were quenched at room temperature in air by pouring the melt on a stainless steel block and pressing with another steel block. The compositions of glass samples prepared are given in table 1.

X-ray diffractograms of the glass samples were recorded using Phillips PW 1140 diffractometer using copper target ($K_\alpha = 1.54 \text{ \AA}$) at room temperature. Infrared transmittance spectra of the glasses were recorded using Perkin-Elmer FT-IS spectrometer model 1605, in the wavenumber range $400-4000 \text{ cm}^{-1}$ at room temperature. ESR spectra of the powdered glass samples were recorded on X-band at room temperature by using JEOL-JM Fe 3

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ESR spectrometer. DPPH was used as standard g marker ($g = 2.0037$). D.c. electrical conductivity of the disc shaped samples of about 2 mm thickness were measured in the temperature range 323–573 K using Keithley 616 type electrometer.

3. Results and discussion

The X-ray diffractograms of G1 to G4 samples show only broad diffuse scattering at low angles characteristic of long-range structural disorder, confirming the amorphous nature of the samples in the composition range studied. IR transmittance spectra of the glasses at room temperature show three fundamental vibrational bands at 820, 618 and 543 cm^{-1} in all glass compositions. A fourth band around 350 cm^{-1} could not be recorded as it was out of range of the apparatus. Due to the hygroscopic character of the powdered glass samples, a water band at 3500 cm^{-1} is also observed in all the glass compositions. Bishay and Maghrabi (1969) reported that in the presence of strong polarizing cations Bi^{3+} can reduce their coordination number (6) from the $[\text{BiO}_6]$ octahedral units and form a glass network into $[\text{BiO}_3]$ pyramidal units which belong to the C_{3v} point group and with four infrared-active fundamental vibrations—a totally symmetric stretching vibration at 840 cm^{-1} , a doubly degenerate stretching vibration at 540–620 cm^{-1} , a totally symmetric bending vibration at 470 cm^{-1} and a doubly degenerate bending vibration at 350 cm^{-1} . The intensity of the observed vibrations is reduced and the transmittance curves broaden significantly due to the nature of disordered structure. Therefore the IR spectra suggest that glass compositions consist of $[\text{BiO}_3]$ pyramidal units. The symmetric vibration bands at 820 and 453 cm^{-1} for the glasses have higher wave numbers compared to the vibration bands of fused Bi_2O_3 (Livage *et al* 1977) suggesting the presence of stronger Bi–O bonds in the glass caused by polarization effects.

The room temperature ESR spectra of all glass compositions are shown in figure 1. Apparently these spectra do not exhibit hyperfine splitting in the parallel feature and only a broad resonance line is observed with varying intensity for different compositions of CuO. The effective g values (g_{eff}) and the peak to peak width (ΔH_{pp}) observed from the spectra are shown in table 2. The values indicate that ΔH_{pp} and effective g value increase with the increase of CuO content in the glass composition. The composition

dependence of ESR line shapes in these glasses may arise due to one or all of the three factors, viz. differing concentration of reduced transition metal ion, phase segregation or different hopping rates of the charge carriers (Livage *et al* 1977; Mandal and Ghosh 1993). The absence of hyperfine structure can be explained on the basis of hopping rate of charge carriers in these glasses. The increase in peak-to-peak width with copper concentration may arise due to the existence of copper ion clusters in the glasses. The interaction between these clusters would give rise to broad ESR peaks. The effective g values (around 2.19) and ΔH_{pp} values obtained in the present investigation are different from the copper bismuthate glasses prepared by rapid quenching technique reported by Hazra and Ghosh (1995) which are given in table 2 for comparison. In the present case glasses are prepared by quenching the melts in air at room temperature. This might be the reason for the difference in g_{eff} and ΔH_{pp} values for nearly equal compositions of copper bismuthate glasses prepared under these two different conditions.

Figure 1. ESR spectra of $x\text{CuO}-(100-x)\text{Bi}_2\text{O}_3$ glass system.

Table 1. Composition of $x\text{CuO}-(100-x)\text{Bi}_2\text{O}_3$ glass system.

Sample	Composition
G1	30CuO–70Bi ₂ O ₃
G2	40CuO–60Bi ₂ O ₃
G3	50CuO–50Bi ₂ O ₃
G4	60CuO–40Bi ₂ O ₃

Table 2. Spin-Hamiltonian parameters of $x\text{CuO}-(100-x) \text{Bi}_2\text{O}_3$ glass system.

Present work			Reference ($\text{CuO}-\text{Bi}_2\text{O}_3$)		
Sample	g_{eff}	ΔH_{pp} (Oe)	Sample	g_{eff}	ΔH_{pp} (Oe)
G1	2.130	370	27.50CuO	2.15	480
G2	2.192	410	35.35CuO	2.15	640
G3	2.199	440	45.70CuO	2.18	1040
G4	2.222	470	55.62CuO	$g_{\parallel} = 2.495$	$A_{\parallel} = 98.45$

D.c. electrical conductivity of all the disc shaped glass samples measured as a function of temperature is shown in figure 2. The general shape of the curve is similar to that reported for $\text{V}_2\text{O}_5-\text{Bi}_2\text{O}_3$ and $\text{WO}_3-\text{P}_2\text{O}_5$ (Ghosh and Chaudhuri 1986) glasses. The d.c. conductivity at any fixed temperature increases with increasing concentration of CuO. The d.c. conductivity of semiconducting oxide glasses for the hopping of polarons in non-adiabatic approximation is given by (Mott 1968; Austin and Mott 1969):

$$\sigma = (vNe^2R^2/kT) C (1 - C) \exp(-2\alpha R) \exp(-W/kT), \quad (1)$$

where the symbols have their usual meanings (Yawale and Pakade 1993). Assuming strong electron lattice interaction the activation energy W can be written as

$$W = W_H + 1/2 W_D \quad \text{for } T > \theta_D/2, \quad (2)$$

$$W = W_D \quad \text{for } T < \theta_D/4, \quad (3)$$

where W_H is the polaron hopping energy and W_D the disorder energy arising from the energy difference of the neighbours between two hopping sites and θ_D the Debye temperature.

To check the nature of hopping conduction mechanism, Sayer and Mansingh (1972) and Murawski *et al* (1979) suggested that when the overlap integral between sites $J_0 \exp(-\alpha R)$ approaches J_0 , i.e. $\exp(-\alpha R) \rightarrow 1$, the hopping is adiabatic and it is mainly controlled by the activation energy. The d.c. conductivity is then given by

$$\sigma = (vNe^2R^2/kT) C (1 - C) \exp(-W/kT). \quad (4)$$

It is observed that the plot of $\log \sigma$ versus $1000/T$ shows a linear behaviour (figure 2) and the conductivity of the glass sample increases with increasing temperature. The calculated activation energies from this plot (figure 2) at a given temperature are given in table 3. The d.c. electrical conductivity of glass samples is found to increase with the increase in the CuO content.

A plot of activation energy versus composition at a temperature of 454 K shows that the activation energy of electrical conduction increases with the percentage increase of CuO. To confirm the nature of hopping conduction mechanism the method suggested by Sayer and

Figure 2. Temperature dependence of d.c. electrical conductivity of $x\text{CuO}-(100-x) \text{Bi}_2\text{O}_3$ glass system.

Mansingh (1972) and Murawski *et al* (1979) is applied. The plot of $\log \sigma$ versus activation energy ' W ' was also investigated at any fixed temperature (454 K) for glasses of different compositions and it was found to be linear, indicating that (4) is applicable. The estimated temperature from the slope ($1/kT$) of the plot is found to be 455 K, which is found to be very close to the chosen fixed temperature. This indicates that the hopping conduction is adiabatic in nature, and that it is mainly controlled by activation energy.

The infrared transmittance studies at different compositions indicate that the structure of the glass consists of $[\text{BiO}_3]$ pyramidal units. The intensity of the vibrations observed for the glasses is reduced and broadened because of their disordered structure. The occurrence of symmetric vibration bands clearly suggests that stronger Bi-O bonds are present in the glass composition. These observations for the quenched glasses are in good agreement with values observed for glasses prepared by rapid quenching technique (Hazra and Ghosh 1995). The observed effective g values (g_{eff}) and peak-to-peak width are changing with composition and is due to exchange interaction between copper clusters. The absence of hyperfine splitting may be due to inhomogeneous broadening and also due to low hopping rates with higher activation

Table 3. Activation energies of $x\text{CuO}-(100-x)\text{Bi}_2\text{O}_3$ glass system at different temperatures.

Glass	Activation energy (eV)		
	416.6 K	454.5 K	500 K
G1	0.836	0.833	0.822
G2	0.777	0.771	0.746
G3	0.763	0.750	0.735
G4	0.709	0.704	0.682

energy in these glasses. At low concentrations of CuO the number of reduced copper ions (Cu^+) is less and hence exchange interaction is more and the rate of hopping of polarons is low, therefore the hyperfine splittings are not clear and the peak to peak width increases with the concentration of CuO.

D.c. electrical conductivity studies clearly indicate that polaronic conduction is increasing with increasing concentration of CuO. The presence of Cu^+ ions between copper clusters (Cu^{2+}) reduces the exchange interaction which is the reason for the broadening of ESR resonance curve. It is also observed that the polaronic conduction is adiabatic in nature. Therefore from the above studies we can conclude that the closed structure of the glass consists of $[\text{BiO}_3]$ pyramidal units due to formation of Bi–O bonds and the conduction arises due to adiabatic hopping of polarons but not due to mobility of copper ions.

4. Conclusions

It is concluded that the glass structure of all the compositions is built up of $[\text{BiO}_3]$ pyramidal units with C_{3v} point group. The observed change in g_{eff} and ΔH_{pp} values with composition of CuO is attributed to reduced exchange interaction between clusters of copper ions. From d.c. electrical conductivity studies it is clear that conduction is due to hopping of polarons between two different valency

states of copper ion and the activation energy decreases with the percentage increase of CuO. The hopping of polarons is adiabatic in nature and is mainly controlled by activation energy.

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References

- Austin I G and Mott N F 1969 *Adv. Phys.* **18** 41
- Bishay A and Maghrabi C 1969 *Phys. Chem. Glasses* **10** 1
- Dumbaugh W H 1978 *Phys. Chem. Glasses* **19** 121
- Dumbaugh W H 1986 *Phys. Chem. Glasses* **27** 119
- Ghosh A and Chaudhuri B K 1986 *J. Non-Cryst. Solids* **83** 151
- Ghosh A and Chakravorty D 1990 *J. Phys. Condens. Matter* **2** 931
- Hazra S and Ghosh A 1995 *Phys. Rev.* **B51** 851
- Komatsu T, Sato R, Imai K, Matusita K and Yamashita T 1988 *Jpn J. Appl. Phys.* **27** L550
- Livage J, Pineau P, Leroy M C and Michand M 1977 *Phys. Status Solidi* **A39** 73
- Mandal S and Ghosh A 1993 *Phys. Rev.* **B48** 9388
- Minami T, Akamatsu Y, Tatsumisago M, Toghe N and Kowada Y 1988 *Jpn J. Appl. Phys.* **27** L777
- Mott N F 1968 *J. Non-Cryst. Solids* **1** 1
- Murawski L, Chung C H and Meckenzie J D 1979 *J. Non-Cryst. Solids* **32** 91
- Onisi M, Kyoto M and Watanabe M 1991 *Jpn J. Appl. Phys.* **30** L988
- Sayer M and Mansingh A 1972 *Phys. Rev.* **B6** 4626
- Tatsumisago M, Tsuboi S, Toghe N and Minami T 1990 *J. Non-Cryst. Solids* **124** 167
- Yuan L R, Kurosawa K, Takigawa Y, Okuda M, Naito H, Nakahigashi K, Nakanishi S and Matsushita T 1991 *Jpn J. Appl. Phys.* **30** L1545
- Yawale S P and Pakade S V 1993 *J. Mater. Sci.* **28** 5451
- Zheng H and Meckenzie J D 1988 *Phys. Rev.* **B38** 7166