

Physical And Transport Properties of CuO-MnO₂-B₂O₃ Glasses

W. J. Gawande¹, S. S. Yawale², S. P. Yawale³

¹Department of Physics, Government Vidarbha Institute of Science and Humanities, Amravati 444604 Maharashtra

^{2,3}Director, Government Vidarbha Institute of Science and Humanities, Amravati Maharashtra

Abstract :

Glasses are very much stronger than organic fibre. Besides glass being a totally non combustible material it greatly improves the fibre endurance of composite. Owing to the technological importance of CuO-MnO₂-B₂O₃ glasses, dc-conductivity measurement with increasing concentration of CuO (in the range of 5-30 mol%) have been reported in the temperature range of 313-573 K in the present study. In addition, the physical properties like density, molecular weight, molar volume, hopping distance, polaron radius and number of ions per cm³ have been reported. A plot of $-\log \sigma$ versus $1/T$ shows two different regions of conduction suggesting two types of conduction mechanisms switching from one type to another occurring at knee temperature. The DC conductivity increases with increase in temperature of the sample and it is composition dependent. Activation energy calculated from both regions (LTR and HTR) is below 1 eV. Thus electrical conduction is electronic. Activation energy in LTR and HTR are temperature independent but composition dependent. The values of effective dielectric constant, polaron binding energy, polaron hopping energy, polaron band width and pre-exponential factor are reported. The nature of hopping conduction is found to be adiabatic. The data has been analysed in the light of polaronic hopping conduction model. The values of dielectric constant at different temperature (313-573K) at a constant frequency of 1 KHz are reported. It is observed that the dielectric constant is independent of temperature upto certain temperature range, but after that the

dielectric constant increases with temperature rapidly. The dielectric constant of all the samples studied is found to be composition dependent. In the glasses studied dipole relaxation phenomenon is observed.

Keywords : CuO- MnO₂-B₂O₃ glasses, physical and electrical properties, adiabatic hopping conduction, dielectric constant.

1. Introduction :

Now a days glasses have a prominent role in the field of electronics and have wide applications in industry, space research, computer memories etc. Since 1954 when the electronically conducting oxide glasses were discovered, glass formation and properties in transition metal oxide systems have been extensively studied due to their important semiconducting behaviour [1-4] Chaudhury et al [5] have discussed in brief the general procedure for making glass ceramic superconductors and some of their physical properties. All the glasses which become superconductors after properly annealing at higher temperatures are in general transition metal oxides (TMO) with copper ions. Ghosh et al [6] discussed the results of dc-conductivity of semiconducting vanadium bismuth oxide, containing 80-95 mol% vanadium pentaoxide in the 300-500 K temperature range on the basis of polaronic hopping model similarly they observed adiabatic hopping conduction. The electrical properties of V₂O₅-B₂O₃ glasses are discussed on the basis of small polaron hopping model by Culea et al [7]. The

charge transfer mechanism plays a dominant role in semiconducting glasses. Dc-conducting and hopping mechanism in $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses has been studied by Yawale et al [8]. The physical and transport properties such as density, hopping distance, polaron radius, dc-conductivity and activation energy are reported by them. The small polaron hopping model is applied to the glass system. Dc-conductivity, density and infrared investigation have been carried out on $\text{Zno-PbO-B}_2\text{O}_3$ glasses by Doweldar et al [9]. In the present work it is decided to measure the variation of physical parameters and dc-electrical conductivity with temperature in $\text{CuO- MnO}_2\text{-B}_2\text{O}_3$ glasses and to study nature of hopping conduction. . The electric relaxation study of $\text{V}_2\text{O}_5\text{-B}_2\text{O}_3$ glasses has been done by Singh et al [23].

2. Experimental Procedure :

2.1 Preparation of glass samples :

The glass samples were prepared in a fireclay crucible. The muffle furnace used was of Heatreat Co. Ltd. (India) operating on 230 volts A.C. reaching upto a maximum temperature of $1500 \pm 10^\circ\text{C}$. Glasses were prepared from A R grade chemicals. Homogenous mixture of an appropriate amounts of CuO , MnO_2 and B_2O_3 (mole%) in powder form was prepared. Then, it was transferred to fire-clay crucible which was subjected to melting temperature (1300°C). The duration of melting was generally two hours. The homogenized molten glass was cast in steel disc of diameter 2 cm and thickness 0.7 cm. Samples were quenched at 200°C and obtained in glass state by sudden quenching method. All the samples were annealed at 350°C for two hours.

2.2 Density Measurement :

The densities of glass samples were measured using the Archimedes principle. Benzene was used as a buoyant liquid. The accuracy in the measurement of density was 0.001 g/cm^3 . The densities obtained d_{expt} were compared with corresponding

theoretical valences, calculated d_{theo} according to the additive rule given by Demkina et al [25]. $d_{\text{theo}} = (\text{Mol\% of CuO} \times \text{density of CuO} + \text{mol\% of MnO}_2 \times \text{density of MnO}_2 + \text{Mol\% of B}_2\text{O}_3 \times \text{density of B}_2\text{O}_3) / 100$

2.3 Electrical Measurement :

The dc resistance of the glass sample was measured by using D.C. microvoltmeter, Systronics 412 India; having an accuracy of $\pm 1 \mu\text{V}$ and input impedance $10 \text{ M}\Omega$, by voltage drop method given by Kher et al [26]. Before electrical measurements all the samples were polished to smooth surfaces using fine quality emery paper. After application of conducting silver paint at either sides, the samples were used for electrical measurements. The silver paint acts like electrodes for all the samples.

2.4 Dielectric Constant :

The dielectric constant of the glass was measured by measuring the capacitance of the samples at constant frequency 1 KHz in the temperature range 313 to 573K. Digital LCR meter 925, systronics made (India), was used for the measurement of capacitance. The accuracy in the capacitance measurement was $\pm 0.1 \text{ pF}$

3 Theory

The dc conductivity of semiconducting oxide glasses for the hopping of polarons in non-adiabatic approximation is given by [1, 2]

$$\sigma = [v_o N e^2 R^2 C (1 - C) \exp(-2\alpha R) \exp(-W/K_B T)] / K_B T \quad (1)$$

Where v_o is the characteristic phonon frequency, α is the electron wave function decay constant, C is mol fraction of sites occupied by an electron, N is the number of metal ions per unit volume, R is the hopping distance (sites spacing) and W is the activation energy. The term $\exp(-\alpha R)$ represents electron overlap integral. When this term approaches unity, the hopping conduction is adiabatic in nature and it is to be mainly controlled by activation energy.

Therefore equation (1) reduces to

$$\sigma = (1 / KT) [v_o Ne^2 R^2 C (1-C) \exp(- W/KT)] \quad (2)$$

The polaron hopping energy [10] W_H is given by

$$W_H = W_P / 2$$

$$1 - \frac{1}{\epsilon_p} = e^2 \left[\frac{1}{4 \epsilon_p r_p} - \frac{1}{R} \right]$$

Where $1/\epsilon_p = 1/\epsilon_\infty - 1/\epsilon_s$, ϵ_p the effective dielectric constant, ϵ_∞ and ϵ_s are the dielectric constant at infinite frequency and static dielectric constants. The polaron radius (r_p) is given by [11]

$$r_p = (1/2) (\pi/6)^{1/3} \times R$$

In generalized polaron model [12], the polaron band width [J] is given by

$$W = W_H - J \quad (3)$$

Where J is related to electron wave function overlap on adjacent sites.

The polaron band width J should satisfy the inequality suggested by Holstein [13]

$$J \geq (2 KTW_H / \pi)^{1/4} (h\omega_{ph} / \pi)^{1/2} \quad (4)$$

Or $J \gg J^*$

> for adiabatic

< for non-adiabatic

$$\text{Where } J^* = (2 KTW_H / \pi)^{1/4} (h\omega_{ph} / \pi)^{1/2} \quad (5)$$

(polaron band width J can be estimated from

$$J \approx e^3 [N (E_F)]^{1/2} / \epsilon_p^{3/2} \quad (6)$$

Where $N (E_F)$ is the density of states at fermilevels.

Table: Physical parameters of CuO- MnO₂-B₂O₃ glasses

4. Results and discussion :

4.1 Physical properties :

The physical parameters such as density (d), molecular weight (M), molar volume (V), hopping distance (R), polaron radius (r_p) and number of ions per unit volume (N) are reported in table 1 for CuO-MnO₂-B₂O₃ glasses. The density, molecular weight and number. of ions per cm³ increases with increasing mol% of CuO but molar volume, hopping distance and polaron radius decreases with increasing mol% of CuO. In glasses

the structure depends on the glass network in which the number of ions enter. In what way they entered and what is the nature of the ions, decides the density of the glass. The increase in the density with increasing

| Glass No. | Composition (mol%) CuO- MnO ₂ -B ₂ O ₃ | Density | | Molecular weight M(gm) | Molar volume V(cm ³ /mol) | No.of ions per cm ³ N(cm ⁻³) x 10 ²² | Hopping distance R(A ^o) | Polaron radius r _p (A ^o) |
|-----------|---|---------------------------|----------------------------|---------------------------|---|--|--|--|
| | | d ^{the} gm/cc | d ^{expt} gm/cc | | | | | |
| G C1 | 5-20-75 | 2.38 | 2.991 | 66.86 | 22.68 | 2.66 | 3.35 | 1.35 |
| G C2 | 10-20-70 | 2.63 | 3.093 | 68.74 | 22.22 | 2.732 | 3.32 | 1.3379 |
| G C3 | 15-20-65 | 2.87 | 3.161 | 69.62 | 22.02 | 2.737 | 3.318 | 1.3371 |
| G C5 | 25-20-55 | 3.36 | 3.360 | 71.37 | 21.24 | 2.86 | 3.27 | 1.31 |
| G C6 | 30-20-50 | 3.60 | 3.477 | 72.25 | 20.77 | 2.91 | 3.25 | 1.30 |

mol% of CuO suggest the decrease in the number of non-bridging oxygen ions. The hopping distance is reduced with the increase in CuO mol% in the glass system. This indicates that the conduction processes becomes fast, because of the small hopping distance the polaron requires smaller time to hop between nearest neighbour place. The values of physical parameters reported are found to be of the order of glasses reported in literature [14-17].

observed that, the conductivity of all the glass samples studied increases with increasing temperature

This plot is found to consists of two distinct straight linear regions called as low temperature regions (LTR) (313 to 413 K) and high temperature region (HTR) (523 to 573 K).

In LTR conductivity increases linearly with increasing temperature at very slow rate where as in HTR conductivity increases linearly with increasing temperature at a faster rate. Obviously two activation energies and two conduction

4.2 Transport Properties :

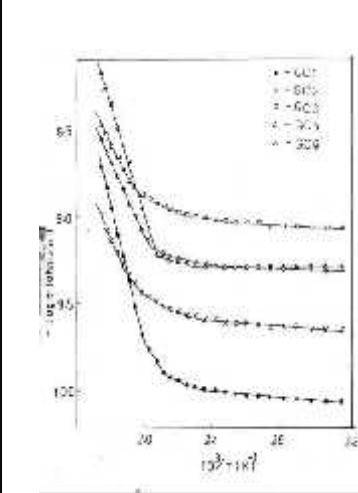


Fig. 1-Temperature Dependence of dc-electrical conductivity for the glasses of different compositions

Table 2 : Transport Properties of CuO-MnO₂-B₂O₃ glasses

D.C. electrical conductivity of the glass samples is measured in the temperature range 313 to 573 K. The value of d.c. conductivity is found to be of the order of 10⁻¹⁰ to 10⁻¹¹ ohm⁻¹ cm⁻¹ at 313 K. Fig 1

mechanisms are associated with electronic conduction in all the glasses studied. The same type of dc conductivity behaviour is reported in literature [8, 18, 19]. The activation energies are obtained from slope of the plot of - log σ versus 1/T in both the regions and reported in table 2. It is observed that the activation energy is temperature independent but depends on composition. The activation energies obtained are found to be of order of borate vanadate and other semiconducting glasses reported in literature [4,20-23]. Activation energy calculated for both regions (LTR and HTR) is found to be less than 1 eV, thus the electrical conduction is electronic.

Table 2 reports the values of activation

shows the plot of - log σ versus 1/T. It is

| Glass No. | Activation energy (eV) | | Effective dielectric constant ε _p | Polaron binding energy W _P (eV) | Polaron hopping energy W _H (eV) | Pre-exponential factor σ _o (ohm ⁻¹ cm ⁻¹) 10 ⁻⁹ | Polaron band width LTR | | Polaron band width HTR | |
|-----------|------------------------|-----------------------|--|--|--|--|------------------------|--------|------------------------|--------|
| | LTR (W _L) | HTR (W _H) | | | | | J eV | J* eV | J eV | J* eV |
| G C1 | 0.0086 | 0.345 | 18.4 | 0.173 | 0.087 | 12.5 | 0.078 | 0.0282 | 0.258 | 0.0308 |
| G C2 | 0.0051 | 0.198 | 14.8 | 0.216 | 0.108 | 8.31 | 0.103 | 0.0307 | 0.090 | 0.0335 |
| G C3 | 0.0069 | 0.181 | 8.2 | 0.392 | 0.196 | 5.24 | 0.189 | 0.0359 | 0.050 | 0.0392 |
| G C5 | 0.0051 | 0.276 | 6.4 | 0.515 | 0.256 | 45.7 | 0.251 | 0.0388 | 0.020 | 0.0424 |
| G C6 | 0.0051 | 0.163 | 7.8 | 0.426 | 0.213 | 10.9 | 0.208 | 0.0385 | 0.050 | 0.0042 |

energy, effective dielectric constant calculated from optical study, polaron binding energy, polaron hopping energy, polaron band width and pre-exponential factor of $\text{CuO-MnO}_2\text{-B}_2\text{O}_3$ glasses. The values of different parameters reported in the table agreed with the values reported for semiconducting glasses in the literature [4, 8, 20-24].

To check the nature of hopping conduction, the condition given by Holstein et al [13] is applied. He has suggested that the polaron band width J should satisfy the inequality equation (4). Accordingly the values of J and J^* are calculated from equation (3) and (5). The value of J for all the glass samples studied in LTR and HTR both are found to be greater than the value of J^* , suggesting the nature of hopping conduction is adiabatic for all the glass samples. The same method was applied to examine the nature of hopping conduction in $\text{V}_2\text{O}_5 - \text{Bi}_2\text{O}_3$ glasses by Ghosh et al [22], $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses by Yawale et al [8], phosphate glasses by Sayer et al [4] and Vanadate glasses by Mori et al [24].

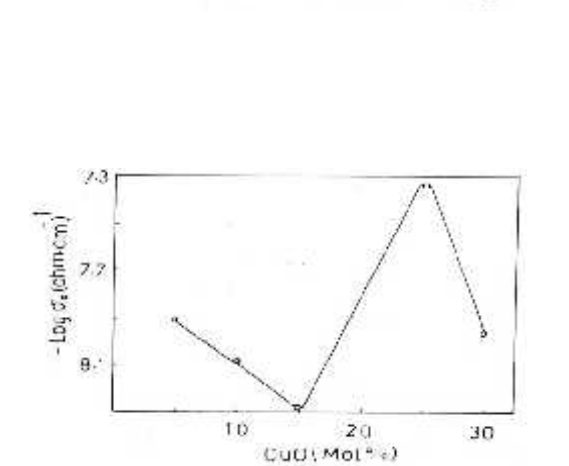
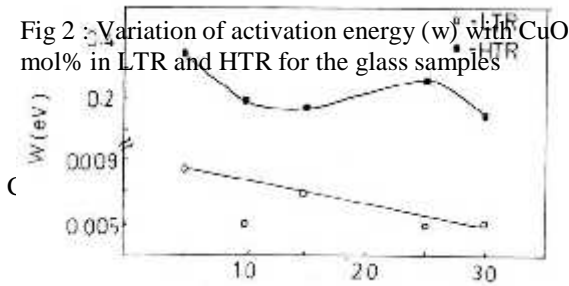
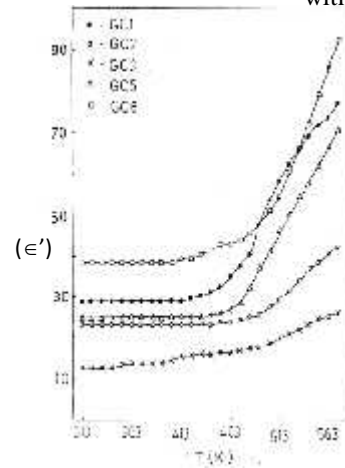


Fig 2 shows the variation of activation energy (w) with CuO mol% in LTR and HTR for the glass samples. Fig 3 shows variation of pre-exponential factor ($-\log A$) versus composition for the glasses studied.

4.3 Dielectric Constant :

The variation of dielectric constant (ϵ') at different temperature (313-573K) at a constant frequency of 1 KHz for the glass samples is shown in Fig. 4. It is observed that the dielectric constant (ϵ') is independent of temperature upto certain temperature range, but after that the dielectric constant

Fig 5 : Variation of dielectric constant with composition at a constant temperature for the glass samples

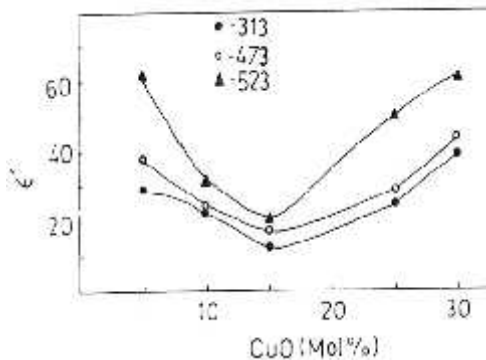


increases with temperature rapidly. A similar trend has been reported for different transition metal oxide glasses by Sayer et al [4], Mansingh

et al [27]. This increase in dielectric constant is partly due to a change in electronic structure and partly due to thermal expansion. In glasses rise of temperature may increase the free carrier density to introduce conduction losses. The change in dielectric constant at high temperature is a characteristics of Debye type relaxation process where symmetrical distribution of relaxation time takes place. The rapid rise is likely to arise from the other sources of polarization possibly from enhanced electrode polarization as temperature rises. More sharp rise of (ϵ') at high temperature was also observed in other oxide glasses by Sunder et al [28] and Singh

et al [23].

The dielectric constant of all the sample studied is found to be composition dependent. Variation of dielectric constant with composition at a constant temperature is shown in figure 5. A dip is observed at 15 mol% of CuO. In these glasses dipole relaxation phenomenon is observed.



5.

Conclusions :

The physical parameters of CuO-MnO₂-B₂O₃ glasses studied are found to be composition dependent and their values reported are found to be of the order of semiconducting glasses. D-C- conductivity of these glasses studied in the temperature range 313-573 k is found to be temperature and composition dependent. The activation energy is temperature independent but composition dependent. The activation energy and other transport properties are found to be in the range of semiconducting glasses. The electrical conduction is electronic. The nature of hopping conduction is found to be adiabatic. The dielectric constant of the glass samples is found to be temperature and composition dependent. In the glasses dipole relaxation phenomenon is observed.

Acknowledgement :

The authors express their sincere thanks to Head, Department of Physics and Director, Govt. Vidarbha Institute of Science and Humanities, Amravati for providing laboratory facilities.

References :

- [1] N. F. Mott, J. Non-Cryst. Solids, 1 (1968) 1.
- [2] L. G. Austin and N. F. Mott, Adv. Phys, 18 (1969) 41.
- [3] E. P. Denton, H. Rawson and J. E. Stanworth, Nature (GB), 173 4413 (1954) 1030.
- [4] M. Sayer and A. Mansingh, Phys. Rev., B6 (1972) 4629.
- [5] B. K. Chaudhury, Bull Mater Sci, 18 1 (1995) 27.
- [6] A. Ghosh and B. K. Chaudhury, Ind J. Phys, 58 A (1984) 62.
- [7] E. Culea and A. Nicula, Solid state Commun (USA), 58 (1986) 545.
- [8] S. P. Yawale and S. V. Pakade, J. Mater Sci., 28 (1993) 5451.
- [9] M. Doweldar, G. M. El-Damrawi and Y. M. Moustafa, J. Phys, 6 42 (1994) 8829.
- [10] L. Murawaski, C. H. Chung and J. D. Mackenzie, J. Non-cryst solids, 32 (1979) 9
- [11] R. H. Clay and M. K. Murthy, J. Am. Ceram. Soc (USA), 53 (1970).
- [12] M. S. Setty, Ind J. Pure & Appl Phys, 17 (1979) 283.
- [13] T. Holstein, Ann Phys 8 (1959) 343.
- [14] W. Soppe, C. V. Marel, W. F. Gunsteren and H. W. Hartog, J Non-cryst, solids, 103 (1988) 201.
- [15] K. V. Damodaran and K. J. Rao, Ceram J., 56 (1989) 3226.
- [16] M. Royle, J. Meckenzie, M. S. Taylor and S. Feiler, J Non-Cryst solids, 17 (1994) 242.
- [17] A Ghosh, Bull Mater Sci, 18 1 (1995) 53.
- [18] J. M. Marshall and A. E. Owen, Phil. Mag, 31 (1975) 1341.
- [19] A. Giridhar and Sudha Mahadevan,

- Bull Mater Sci., 12 2 (1989) 107.
- [20] A. N. Nassar, Ind J. Pure Phys., 20 (1982) 337.
- [21] A. R. Kulkarni, H. S. Maiti and A. Paul, Bull Mater Sci., 6 (1984) 207.
- [22] A. Ghosh and B. K. Chaudhury, J. Non-Cryst Solids, 83 (1986) 151.
- [23] B. Singh and P. S. Tarsikka , Ind J. Pure Appl Phys, 26 (1988) 660.
- [24] H. Mori, J Igarashi and H. Sakata, J Ceram Soc (Japan), 101 (1993) 1315.
- [25] L. I. Demkina, Structure of glass (New York), 2 (1960) 4.
- [26] V. G. Kher and C. S. Adgaonkar, Ind J Pure Appl Phys, 10 (1972) 902.
- 27] Mansingh A, Dhawan V K and Sayer M Phil Mag, 1348 8(1983) 215.
- [28] Sunder, H G K and Rao K J Pramana, 19(1982) 125.