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CuO-MnO2-B2O3 Physical Glasses and Transport Properties

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Abstract

Glasses have a longer lifespan than biological materials. The use of glass in the composite not only increases the longevity of the fibers, but also renders them indestructible in the event of a fire. Recent investigation on CuO-MnO2-B2O3 glasses with increasing CuO content (from 5-30 mol%) reveals dc-conductivity readings in the 313-573 K temperature range. Some of the physical parameters that have been made public include density, molecular weight, molar volume, hopping distance, polaron radius, and number of ions per cm3. One may observe, for instance, that there are two distinct conduction areas, with the transition happening at knee temperature, if one plots -log against 1/T. Composition and temperature are also potential causes of elevated DC conductivity. The activation energy is demonstrated to be less than 1 eV by combining data from the LTR and the HTR. Electrical transmission necessitates electronic gadgets. LTRs and HTRs' activation energy is composition- and not temperature-dependent. We provide you the effective dielectric constant, the binding energy, the hopping energy, and the band width of polarons. It is shown that conduction happens adiabatically during hopping. A model of polaronic hopping conduction has been used to analyze the data. Over a broad temperature range (313-573K), we provide the values of the dielectric constant at 1 KHz. Research has shown that the dielectric constant is constant up to a certain temperature.

When heated, the dielectric constant increases dramatically. The dielectric constant was found to change depending on the kind of sample used. The investigated glasses exhibit a phenomenon known as dipole relaxation.

CuO-MnO2-B2O3 glasses are characterized by their dielectric constant, adiabatic hopping onduction, and other physical and electrical properties.

1. Introduction :

Glasses now play an important part in electronics and find use in many different fields, including manufacturing, space exploration, computer memory, and many others. Glass formation and characteristics in transition metal oxide systems have been widely investigated because of their crucial semiconducting behavior [1-4] since the electrically conducting oxide glasses were found in 1954. The production process and some of the physical features of glass ceramic superconductors have been briefly described by Chaudhury et al [5]. After adequate annealing at higher temperatures, all glasses containing transition metal oxides (TMO) with copper ions transform into superconductors. According to the polaronic hopping model, Ghosh et al. [6] reported adiabatic hopping conduction in a semiconducting vanadium bismuth oxide having 80-95 mol% vanadium pentaoxide in the 300-500 K temperature range. Based on the tiny polaron hopping model, Culea et al. [7] analyze the electrical characteristics of V2O5-B2O3 glasses. The

Semiconducting glasses rely heavily on their charge transfer mechanism. Yawale et al. [8] examined the dc-conducting and hopping process in Bi2O3-B2O3 glasses. They detail the material's density, hopping distance, polaron radius, dc-conductivity, and activation energy, among other physical and transport parameters. The glass system is used as an example of the tiny polaron hopping model. Doweldar et al. [9] studied the dc-conductivity, density, and infrared properties of Zno-PbO-B2O3 glasses. The purpose of this work is to investigate the hopping conduction mechanism in CuO-MnO2-B2O3 glasses by measuring the temperature dependence of physical characteristics and dc-electrical conductivity. Singh et al. [23] have investigated the effect of V2O5-B2O3 glasses on electric relaxation.

2. Experimental Procedure :

2.1 Preparation of glass samples :

The glass samples were prepared ina fireclay crucible. The muffle furnace used was of Heatreat Co. Ltd. (India) operatingon 230 volts A.C. reaching upto a maximum temperature of 1500 ± 10^{o}C.

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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^{O}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^{O}C and obtained in glass state by sudden quenching method. All the samples were annealed at 350^{O} 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_{theo} = (Mol% of CuO x density of CuO + mol% of MnO2 x density of MnO_2 + Mol% of B_2O_3 xdensity of B_2O_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 $\pm 1\ \mu V$ and input impedence 10 MΩ, 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 measuredbymeasuring the capacitance ofthe samples at constantfrequency 1 KHz in the temperature range 313 to 573K.Digital LCR meter 925, systronics made (India),wasusedfor the measurement of capacitance. The accuracyinthecapacitance measurement was ±0.1 pF

3 Theory

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

$$\sigma = [\ \nu_o Ne^2R^2 C (1 - C) \exp(-2\alpha R) \exp(-W/K_BT)] / K_BT \quad (1)$$

Where ν_o is the characteristic phonon frequency, α is the electron wave function decay constant, C is mol fraction of sitesoccupied 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. Whenthis 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

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

The polaron hopping energy [10] W_H isgiven by

$$W_H = W_P / 2$$

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

(polaron band width J can be estimated from

$$J \approx e^3 [\ N (E_F)]^{½} / \varepsilon_p^{3/2} \quad (6)$$

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Where N (E_F) is the density of states atfermilevels.

1

1

= e^2 [—

- —] / 4 ε_p

r_P R

Where $1/\varepsilon_p = 1/\varepsilon_\infty - 1/\varepsilon_s$, 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]

$$r_p = (½) (\pi/6)^{1/3} \times R$$

In generalized polaron model [12], thepolaron band witdth [J] is given by

Results and discussion :

4.1 Physical properties :

The physical parameters such asdensity (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- MnO_2-B_2O_3 glasses. The density, molecular

3

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

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]

$J \gtrless (2 KTW_H / \pi)^{1/4} (h\omega_{ph} / \pi)^{1/2}$ (4) Or $J \lessgtr J^*$

> for adiabatic

< for non-adiabaticweight and number. of ions per cm

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 networkin 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_2O_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. Thehopping 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 reportedin literature [14-17].

4.2 ansport Properties :

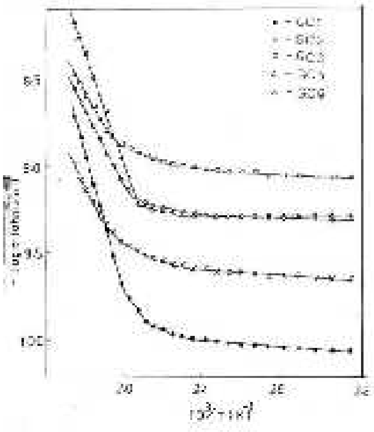

Fig. 1-Temperature Dependence of dc-electrical conductivity forthe glasses of different compositions

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Thus, when temperature is increased, the conductivity of all the glass samples tested rises

Two separate straight linear zones, designated as low temperature regions (LTR; 313–413 K) and high temperature regions (HTR; 523–573 K), are shown in this figure.

The conductivity of LTR materials grows linearly with temperature at a relatively slow pace, whereas the conductivity of HTR materials increases linearly with temperature at a quicker rate. Two activation energies and two conduction energies are

Table 2 : Transport Properties of CuO-MnO_2-B_2O_3 glasses D.C. electricalconductivity of the glasssamples is measured inthe temperature range 313 to573 K. Thevalue of d.c. conductivity isfound to be of the order of 10^{-10} to 10^{-11} ohm^{-1} cm^{-1} atare associated with electronic conduction in all the glasses studied. Thesame type of dc conductivity behaviour isreported in literature [8, 18, 19]. Theactivation 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.

shows the plot of - log σ versus 1/T. It is Table 2 reports the values of activation

Glass No.	Activation energy W(eV)		Effective dielectric constant ε_p	Polaron binding energy W_P(eV)	Polaron hopping energy W_H(eV)	Pre-exponential factor σ_o (ohm x 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		
GC1	0.0086	0.345	18.4	0.173	0.087	12.5	0.078	0.0282	0.258	0.0308		
GC2	0.0051	0.198	14.8	0.216	0.108	8.31	0.103	0.0307	0.090	0.0335		
GC3	0.0069	0.181	8.2	0.392	0.196	5.24	0.189	0.0359	0.050	0.0392		
GC5	0.0051	0.276	6.4	0.515	0.256	45.7	0.251	0.0388	0.020	0.0424		
GC6	0.0051	0.163	7.8	0.426	0.213	10.9	0.208	0.0385	0.050	0.0042		

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energy, effective dielectric constant calculated from optical study, polaron binding energy, polaron hopping energy, polaron band width and pre-exponentialfactor of CuO-MnO_2-B_2O_3 glasses. Thevalues of different parameters reported in the table agreed with the values reported for semiconducting glasses in the literature [4,

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 ($-\log\sigma_0$)versus composition for the glasses studied.

8, 20-24].

Dielectric Constant :

To check the nature of hoppingconduction, 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

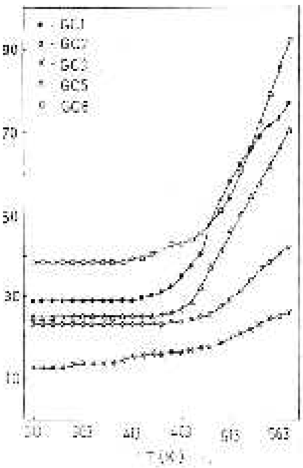
The variation of dielectric constant ($\in$') atdifferent temperature (313-573K) at a constant frequency of 1 KHz for the glass samples is shown in Fig. 4. It is observed that the dielectric contant ($\in$')is

independent of temperature upto certaintemperature range, but after that the

both are found to be greater than the valueof J*, suggesting the nature of hoppingconduction is adiabatic for all the glass samples. The same method was applied toexamine the nature of hopping conductionin V_2O_5 – Bi_2O_3 glasses by Ghosh et al [22],Bi_2O_3-B_2O_3 glasses by Yawale et al [8],phosphate glasses by Sayer et al [4] andVanadate glasses by Mori et al [24].

Fig 5 : Variation of dielectric constantwith composition at aconstanterature for the lass samples

increases withtemperature rapidly. Asimilar trendhasreported fordifferent transition metaloxide glassesby Sayer e



t al[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 ($\in$') at high temperature was also observed in other oxide glasses by Sunder et al [28] and Singh

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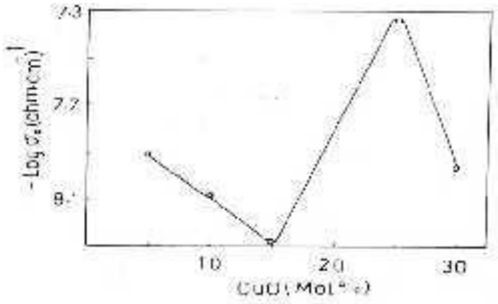

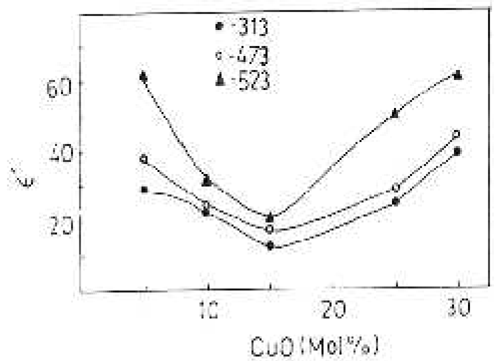

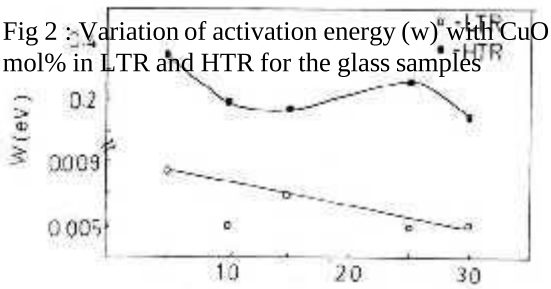

Fig 2 : Variation of activation energy (w) with CuO mol% in LTR and HTR for the glass samples

The dielectric constant of all the sample studied is found to be composition dependent. Variation of dielectric constantwith 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.

Conclusions :

Values given for physical properties of CuO-MnO2-B2O3 glasses are found to be on the order of semiconducting glasses, and these parameters are found to be composition dependent. In the region of 313-573 k, the D-C- donductivity of these glasses is observed to vary with both temperature and composition. Activation energy varies with composition but is independent of temperature. The transport characteristics, including the activation energy, are found to be comparable to those of semiconducting glasses. Electrical current is conducted electronically. It is discovered that hopping conduction is adiabatically conducted. Glass samples are discovered to have a dielectric constant that varies with both temperature and composition. The phenomena of dipole relaxation may be seen in glasses.

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