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Physical and electrical properties of semiconducting Fe_2O_3-V_2O_5-B_2O_3 glasses

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The physical and electrical properties of semiconducting oxide glasses with composition $x$$Fe_2O_3$ (70-x)V_2O_5.30 B_2O_3, (0≤ x ≤20) have been investigated. The glasses were prepared by normal melt quench technique. The conduction mechanism of these glasses was found to be adiabatic. The experimental data have been analyzed in the light of small polaron hopping theory. The density and molar volume of the present glass system are found to depend on Fe_2O_3 substitution. The dc conductivity was measured in the temperature range 313-473 K. The conductivity of all the glass compositions decreases with increasing Fe_2O_3 content and increases with increase in temperature. The observed value of conductivity at 430 K lies in the range 5.559×10^{-2} to 0.957×10^{-2} Sm^{-1}. The various parameters such as activation energy, average site separation between transition metal ions, and polaron radius have been calculated and found consistent with Mott's small polaron hopping theory.

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1. Introduction

It is well established that oxide glasses containing transition metal ions such as Fe, V, Co, etc. exhibit semiconducting properties [1-2]. The semiconducting behaviour in these glasses is due to the existence of transition metal ions in more than one valance state e.g. Fe^{2+} and Fe^{3+} [3-4]. The electron phonon interaction in these glasses is strong enough to form small polarons and the electrical conduction takes place by hopping of polarons from low valance state to high valance state of transition metal ions [3-5]. The conduction mechanism in most of the glasses containing less than 50 mol% V_2O_5 is considered to be non-adiabatic [6] while for V_2O_5>50 mol %, conduction is considered to become adiabatic [1]. These glasses have drawn much attention due to their potential in switching and memory devices, transducers and cathode material for making optical fibers etc [5,7,8]. Although sufficient work on vandate glasses with P_2O_5, TeO_2, WO_3 as a glass former have been reported [9,10], however there is a few report on vanadium glasses prepared with B_2O_3 as a glass former [11]. Recently the researchers have focused their main attention to study the electrical behaviour of the semiconducting glasses containing two kinds of transition metal ions [10]. In the present work we prepared semiconducting oxide glasses with B_2O_3 as glass former having iron and vanadium as transition metal ions. The main objective of the present paper is to study the effect of temperature and composition on electrical behaviour of as prepared glasses by varying the relative proportion of Fe and V ions, keeping total transition metal oxide concentration fixed at ≈ 70 mol %.

2. Experimental

The glass samples of compositions $x$$Fe_2O_3$(70-$x$) V_2O_5.30B_2O_3; x=0, 5, 10, 15 and 20 were prepared from analytical reagent grade Fe_2O_3, V_2O_5, H_3BO_3 chemicals. The weighted quantities of the starting materials of 15 gm. were properly mixed and then melted in a porcelain crucible for 1h in muffle furnace at 1300 K in air .The melts were then quenched by pouring them in between two thick carbon plates. The density of glasses was determined at room temperature by using Archimede's principle with Xylene as a buoyant liquid.

As prepared glasses were polished and cut into plates of nearly 1×1 cm size and about 1 mm in thickness for electrical measurement. Silver electrodes were deposited on both surfaces of the polished samples. The electrical conductivity was carried out on a Keithley electrometer (Model-617 A) in the temperature range 313-473 K.

3. Results and discussion

3.1 Density and molar volume

The X-ray diffraction pattern of iron doped vanadium borate glasses shows no peaks which indicate the amorphous nature of the glass samples. The density of each composition was determined at room temperature by using Archimede's principle. The calculated values of density, listed in Table 1, indicate that density increases with increasing iron content. The relationship between the density and composition of an oxide glass system can be expressed in terms of apparent volume V_M.

Table 1. Chemical composition and physical properties of Fe_2O_3 -V_2O_5 -B_2O_3 glasses

Glass ID	Glass composition			Density D (gm/cm^3)	Molar Vol. V_M (cm^3)
	Fe_2O_3	V_2O_5	B_2O_3		
BVF-0	0	60	30	2.98	49.72
BVF-1	5	65	30	2.12	47.14
BVF-2	10	60	30	3.29	44.36
BVF-3	15	55	30	3.40	42.60
BVF-4	20	50	30	3.51	40.95

Fig.1 shows that molar volume decreases with increasing Fe_2O_3 mole percent. These results are due to the replacement of heavier 'Fe' ions by lighter vanadium ions and in good agreement with the results reported [12] earlier.

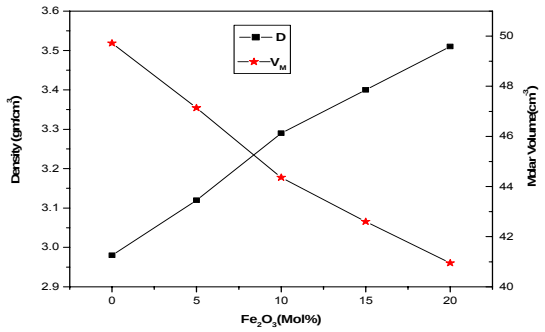

Fig. 1. Variation of the density and molar volume with Fe_2O_3 mol%.

3.2 DC conductivity

The dc conductivity of various glasses was measured in the temperature range 313-473 K. The temperature dependence of dc conductivity for different glass compositions is shown in Fig 2. All glasses show smooth variation of DC conductivity with reciprocal temperature, indicating temperature dependent activation energy W, which is a characteristic of SPH conduction in semi-conducting glasses. The activation energy is calculated from the slope of the linear portion of Fig. 2 and listed in Table 2.

The composition dependence of the dc conductivity at 330 K is shown in Fig. 3, which suggests that with increasing Fe_2O_3 contents the electrical conductivity decreases. It implies that Fe ions in the present glass system hinder the carrier transport [13]. This happens as Fe_2O_3 is not a glass former. In the glass network, Fe ions are isolated which give rise to obstruction in the hopping of electrons due to lack of oxygen bonds. A similar trend is reported in V_2O_5 – Fe_2O_3 -TeO_2 [14], P_2O_5 – V_2O_5 – Fe_2O_3 [9] and V_2O_5 – Mno – TeO_2 [15] glasses.

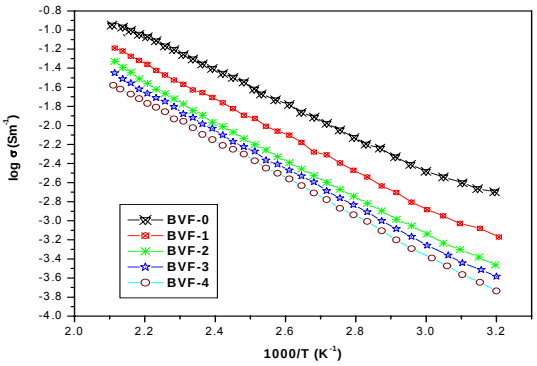

Fig. 2 Variation of logσ with 10^3 /T (K^{-1}) for Fe_2O_3 - V_2O_5-B_2O_3 glasses.

Table 2. Variation of electrical properties of Fe_2O_3 -V_2O_5 -B_2O_3 glasses.

Glass	W (eV)	$\log\sigma_0$ $(\Omega\ m)^{-1}$	σ_{330} $(\Omega\ m)^{-1}$	σ_{430} $(\Omega\ m)^{-1}$
BVF-0	0.34	2.719	3.357×10^{-3}	5.559×10^{-2}
BVF-1	0.37	2.793	1.218×10^{-3}	2.666×10^{-2}
BVF-2	0.39	2.812	0.650×10^{-3}	1.548×10^{-2}
BVF-3	0.40	2.789	0.475×10^{-3}	1.230×10^{-2}
BVF-4	0.41	2.751	0.364×10^{-3}	0.957×10^{-2}

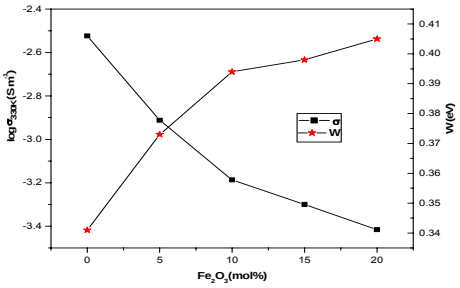

Fig. 3. Variation of dc conductivity, and activation energy at T=330K with iron contents.

As seen in Fig. 3, the activation energy increases with increasing Fe_2O_3 content. It is also observed that the activation energy shows negative correlation with conductivity, which is consistent with small polaron hopping theory. The low value of activation energy and high value of dc conductivity in the present set of glasses are similar to those of CuO - V_2O_5-TeO_2 [10], CdO – V_2O_5 [16] glasses.

For comparison sake, DC conductivity for all glass samples at two different temperatures is plotted in Fig.4. As seen from the figure, conductivity increases with

increase in temperature indicating typical semiconducting behaviour. The concentration of Iron and Vanadium ions was computed (listed in Table 3) using the following formula [6]:

$$N = 2\left[\frac{dW_t}{M_{W_t}}\right]N_A \qquad (1)$$

where d is density, Wt is the weight fraction and M_{Wt} is molecular weight of respective ions (Fe and V). N_A is the Avogadro number.

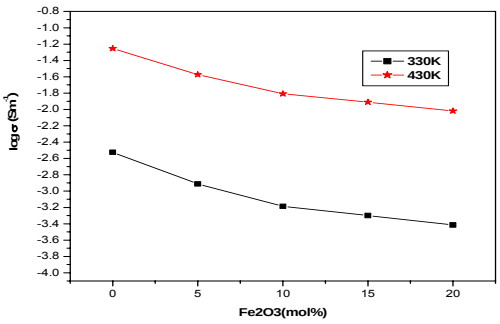

Fig. 4 Variation of dc conductivity with Fe_2O_3 mol% at T=330 and 440 K.

The mean site separation (R) between transition metal ions (assuming homogenous distribution of Transition ions in the glass volume) was calculated by using the relation [17, 18] (listed in Table 3)

$$R = \left(\frac{1}{N}\right)^3 \qquad (2)$$

where 'N' represents the concentration of total transition ions in glass composition.

Table 3. Hopping parameters of Fe_2O_3-V_2O_5-B_2O_3 glasses.

Glass	N_{Fe2O3} ($\times10^{23}cm^{-3}$)	N_{V2O5} ($\times10^{23}cm^{-3}$)	$N_{Fe2O3+V2O5}$ ($\times10^{23}$ cm^{-3})	R (nm)
BVF-0	0.0000	0.1691	0.1695	0.389
BVF-1	0.0127	0.1660	0.1787	0.382
BVF-2	0.0271	0.1628	0.1899	0.374
BVF-3	0.0423	0.1554	0.1977	0.369
BVF-4	0.0587	0.1470	0.2057	0.364

Fig. 5 shows the variation of activation energy (W) with mean site separation (R). It is observed that with increase in site separation between transition metal ions the activation energy decreases. This is consistent with the results obtained in MO_3 – TeO_2 [19] and V_2O_5 – Fe_2O_3 – TeO_2 [14].

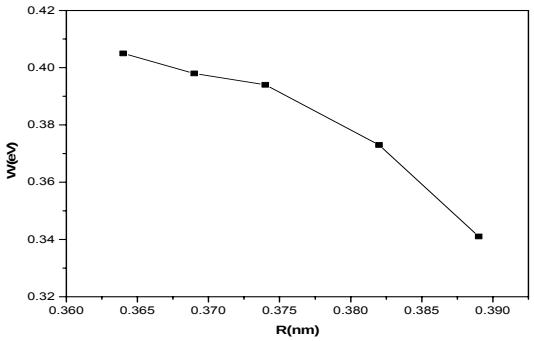

Fig. 5. Variation of the activation energy 'W' with average ion separation 'R'.

At high temperature ($T > \theta_D/2$), the conduction Mechanism in TI-glasses is generally describes by Mott-Holstein SPH Model [20, 21]. In this model, the conduction process is considered in terms of phonon assisted hopping of small polarons between localized states. The DC conductivity in Mott's model for the nearest neighboring hopping in non-adiabatic regime at high temperature ($T > \theta_D/2$) is given as

$$\sigma = \frac{\nu_0 N e^2 R^2}{kT} C(1-C) \times e^{(-2\alpha R)} \times e^{\left(\frac{-W}{kT}\right)} \qquad (3)$$

where W is activation energy for hopping conduction, ν_0 is optical phonon frequency; R is the average site separation. 'α' is tunneling factor (ratio of wave function decay), N is density of T.M.I., C is fraction of reduced TMI's. Assuming that a strong electron-phonon interaction exists, the activation energy W is the result of polaron formation of binding energy W_P and an energy difference W_D that might exist between the initial and final sites due to variation in the local arrangements of ions. Austin and Mott have shown that $W = W_H + W_D/2$ for $T > \theta_D/2$ and is $\approx W_D$ for $T < \theta_D/4$, with $W_H = W_P/2$ is the polaron hopping energy. W_D is disorder energy arising from the energy difference between two sites due to variation in the local arrangement of ions. θ_D is Debye temperature which was calculated by estimating departure from linear plot of dc conductivity versus inverse temperature Fig. 2 shows linear temperature dependence up to critical temperature $\theta_D/2$ and thereafter deviates from linearity. This is consistent with SPH [20, 22] .The Debye the temperature for the present glass system were obtained in the range 672-692 K. and listed in Table 4. The value of optical phonon frequency ν_0 was calculated by using the relation

$k\theta_D = h\nu_0$, where k is Boltzmann constant and h is planck's constant and is also summarized in Table 4.

Table 4. Polaron hopping parameters of Fe_2O_3 -V_2O_5 -B_2O_3 glasses.

Glass (nm)	θ_D	ν_0	N (E_F)	r_P
		($\times10^{13}$ Hz)	($\times10^{21}$ eV^{-1} cm^{-3})	
BVF-0	672	1.40	11.92	0.15
BVF-1	676	1.41	11.57	0.15
BVF-2	684	1.42	11.69	0.15
BVF-3	686	1.43	11.87	0.14
BVF-4	692	1.44	12.07	0.14

In TMO glass, conduction mechanism may be either adiabatic or non adiabatic, depending upon the probability of successful 'jumps' of carrier from one center to the other. For adiabatic conduction, the term $e^{-2\alpha R}$ of equation (1) is ≈1 [1, 18] then from equation (1) the conductivity (σ) and pre-exponential factor (σ_0) can be expressed as follows:

$$\sigma = \frac{\nu_0 N e^2 R^2}{kT} C(1-C) \times e^{\left(\frac{-W}{kT}\right)} \quad (4)$$

and

$$\sigma_0 = \frac{\nu_0 N e^2 R^2}{kT} C(1-C) \quad (5)$$

The value of log σ_0 was computed from the intercept of the conductivity Vs temperature curve (fig. 2). The observed values (listed in Table 2) are found to be independent of Fe_2O_3 content as shown in Fig. 6. It confirms the adiabatic SPH for the present glass system. Therefore, in adiabatic regime (at a given temperature) conductivity depends completely on activation energy as

$$\sigma = \sigma_o e^{\frac{-W}{kT}} \quad (6)$$

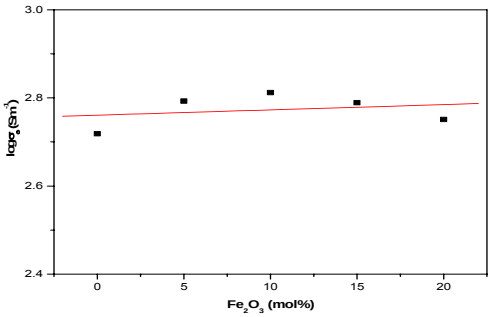

Fig. 6 Variation of log σ_0 with iron contents

Fig. 7 shows the plot between log σ (Sm^{-1}) and W(eV) at 430 K and its slope is found to be equal to 11.67 $(eV)^{-1}$ This is almost same as the theoretical slope for the adiabatic hopping $(\tan\theta = -\frac{1}{2.303}kT)$ which is equal to 11.70 $(eV)^{-1}$. The equivalent temperature corresponding to the experimental value of slop is = 431 K. These two results again confirm the adiabatic SPH conduction in the present glass system.

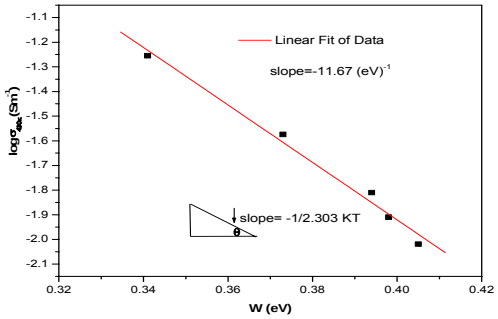

Fig. 7 Variation of log σ with activation energy at 430K.

Holstein and co-workers have investigated a general polaron hopping model assuming W_D = 0, covering both the adiabatic and non-adiabatic hopping processes. On the basis of molecular crystal model the dc conductivity has been deduced for non adiabatic hopping as,

$$\sigma = \left(\frac{3e^2 N R^2 J^2}{2kT}\right)\left(\frac{\pi}{kTW_H}\right)^{\frac{1}{2}} e^{\frac{-W_H}{kT}} \quad (7)$$

while for adiabatic hopping it has been shown that

$$\sigma = \left(\frac{8\pi e^2 N R^2 \nu_0}{3kT}\right) e^{\frac{-(W_H - J)}{kT}} \quad (8)$$

where N is the site concentration and J is the transfer integral related to the electron wave function overlap on adjacent sites. The condition for the nature of hopping has also been proposed in this model and is expressed for adiabatic hopping as

$$J > \left(\frac{2kTW_H}{\pi}\right)^{\frac{1}{4}} \left(\frac{h\nu_0}{\pi}\right)^{\frac{1}{2}} \quad (9)$$

and

$$J < \left(\frac{2kTW_H}{\pi}\right)^{\frac{1}{4}} \left(\frac{h\nu_0}{\pi}\right)^{\frac{1}{2}} \quad (10)$$

for non adiabatic hopping, with the condition for the existence of a small polaron being $J \le \frac{W_H}{3}$. Bogomolov

et al. [23] have calculated the polaron radius r_P for a non-dispersive system of frequency ν_0 is given by

$$r_P = \left(\frac{\pi}{6}\right)^{\frac{1}{3}} \frac{R}{2} \tag{11}$$

The density of states N (E_F) near Fermi level is given by the following relation [14, 15]

$$N(E_F) = \frac{3}{4\pi R^3 W} \tag{12}$$

Using value of R and W from Table 2 the value of N(E_F) calculated (listed in Table-3) and found to be of order of 10^{21} eV^{-1} cm^{-3}. These values are in reasonable agreement with localized states [24, 25].

4. Conclusions

Density, Molar volume and the DC conductivity of $xFe_2O_3(70\text{-}X)V_2O_5.30B_2O_3$, ($0 \leq x \leq 20$) glasses have been investigated. The density of all the glass samples increases with increasing Fe_2O_3 content. The molar volume is found to decrease with increase in iron concentration. The DC conductivity decreases with increasing Fe_2O_3 mol%. The conductivity shows prominent positive correlation with temperature, indicating temperature dependent activation energy, characteristic of SPH mechanism. The DC conductivity at 430 k varies between 5.559×10^{-2} and 0.957×10^{-2} Sm^{-1} for $0 \leq x \leq 20$. The electrical conduction in high temperature regime ($T > \theta_D/2$) was confirmed to be due to adiabatic small polaron hopping of electrons between transition ions.

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