Int. Res. J. of Science & Engineering, 2014; Vol. 2 (5): 161-166. ISSN: 2322-0015

RESEARCH ARTICLE

Transport properties of Vanadium Borate Glasses

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Manuscript Details

Received : 28 May, 2014
Revised : 14 June, 2014
Accepted: 25 August, 2014
Published: 05 September, 2014

ISSN: 2322-0015

Editor: Dr. Arvind Chavhan

Cite this article as:
Dhote DS. Transport properties of Vanadium Borate Glasses, *Int. Res. J. of Sci. & Engg*., 2014; 2 (5):161-166.

Acknowledgement:

The authors are very much thankful to the Director and Head, Department of Physics, Govt. Vidarbha Institute of Science and Humanities, Amravati for providing laboratory facilities.

ABSTRACT

Glasses of V_2O_5 and B_2O_3 having mol % 5-25 of V_2O_5 are prepared and dc electrical conductivity is measured in the temperature range 303 to 523K. The conductivity is calculated by measuring the dc resistance of the samples at different temperatures. The conductivity of these glasses varies from 10 to 10" (ohm-cm)"1. The nature of hopping conduction is examined by the condition given by Holstein. According to Holstein, the polaron band width J should satisfy the inequality (J < J*). Accordingly the values of J and J* are calculated and reported. The values of J for the glass sample studied are found to be less than J* suggesting that the nature of hopping conduction is non-adiabatic. The values of density of states at Fermi level obtained are found to be reasonable for localized states.

Keywords: V_2O_5, Electrical Conductivity, non adiabatic.

INTRODUCTION

Electrical conductivity of the material is a important factor while studying the electrical properties. It has gain the prime importance because of exploitation of the glasses m the, state devices and other industrial applications. The switching and memory devices, transducers, computer memories, memory diodes might be cheaply produced with glass. Thus glass became an ordinary electronic material. The properties and characteristics of these materials are important from two main points of view. Electrical engineer considers these materials primary as components in electrical circuit having specified property and characteristics with regards to electrical measurements. The physicist considers these properties in terms of quantitative understanding of the electronic and ionic behavior (Gawande *et al*., 2014; Denton *et al*., 1954a; 1954b; Meckenie, 1966).

Electrical conductivity of glasses varies with composition and increases with temperature. High alkali contents give high conductivity. The amorphous glassy solid finds many advantages over crystalline solids. The applications of glasses are increasing rapidly in solid state devices, structurally glasses are amorphous and electrically insulators. However the electronic band structure of these disordered solids can lead to

semiconductor and metal behavior under different conditions (Kulkarni *et al*., 1984; Linsley *et al*., 1970). When several transition metal oxides, such as V_2O_5, WO_3, Fe_2O_3. etc., are heated with glass formers semiconducting glasses are formed on quenching the melt Many research workers (Pakade *et al*., 1988; Ghosh and Chaudhuri, 1984) have studied the various glass systems like V_2,O_5.-B_2 O_3,. V_2O_3-P_2O_5 V_2 O_5 - TeO. etc. with an intention to know the electrical conduction mechanism In many glass systems it has been observed that the thermal activation energy plays a dominant role in electrical conduction.

The glass systems with P_2 O_5 namely V_2O_5-P_2,O_5 and WO_3-P_2 O_5 show adiabatic hopping conduction (Sayer and Mansingh, 1984) where as V_2 O_5 - TeO and Fe_2O_3-P_2 O_5 exhibit non adiabatic hopping conduction (Ghosh and Chaudhuri, 1986). Pakade *et al*. (1986) have studied the activation energies of V_2O_5-P_2O_5 glasses and effect of past electric field on the dc conductivity of $80V_2O_5$-$20P_2O_5$ semiconducting glass Yawale *et al*. (1992); Singh and Tarasikka (1988) and Ghosh and Chaudhury, (1986) have reported the electrical conduction in V_2,O_5.-B_2 O_3, and V_2,O_5.-B_2 O_3, glasses, respectively. In such glasses hopping conduction of small polarons between V^{4+} and V^{5+} have been observed, suggesting that, the conduction is electronic and the activation energy is temperature dependent. In the present work, the electrical conductivity is studied with an intention to know the conduction mechanism in the V_2,O_5.-B_2 O_3 glasses.

MATERIALS AND METHODS

(a) Preparation of Glasses

Glasses were prepared from AR grade chemicals of V_2,O_5 and B_2 O_3 of different compositions. Appropriate amounts in mol% of V_2O_5 and B_2 O_3 in powder f were weighed on K-Roy monopan balance having accuracy of $\pm$0.00001gm Repeated grinding of mixture was done to ensure homogenization. Homogeneous mixture was r transferred to fire clay crucibles which was then subjected to melting in an automatic; controlled muffle furnace, at temperature ranging from 1000 to 12000 $\pm$ 10°C. The duration of melting was generally four hours. The homogenized molten mass was cast in steel discs of 2.5 cm length and 0.7 cm thickness. The samples were quenched at 200^{0}C to avoid cracking and shattering of glass.

After quenching, all samples were immediately transferred to a annealing furnace Samples were annealed at 100 C for two hours. The effect of annealing is to remove air bubbles or cavities, if any, which may be formed by sudden quenching. All glasses after annealing were subjected to finishing processes such as cleaning and polishing Sufficient number of glass samples were prepared from the same batch of' compositions, for attaining exact parallel and plane surfaces of glasses, a fine lapping paper was used. A conducting silver paint was applied to either side of glass samples. All the samples were baked at 80^{0}C for two hours, for removal of mechanical stresses, if any developed during poll slung. The general formula is XV_2 O5- (100-X)B_2O_3 glasses can only be formed in the suggested V.O, compositions. Increasing the VOs composition beyond 25 mol%, increases the cavity in the glass matrix therefore above mentioned mol5 are selected for the present study. Amorphous behavior of the samples is checked by obtaining the X-ray spectra on Philips X-ray spectrophotometer.

b) Measurement of dc conductivity

DC electrical conductivity of all glass samples under study was measured by finding its resistance. The resistance of the sample was measured by using a method adopted by Yawale and Pakade (1993) and kher *et al*. (1972).

The circuit consists of a dc regulated power supply of 5 volts and a digital Dc-micro voltmeter (Systronic-412. India) having input impedance of 10M O to measure the resistance of the glass sample, standard resistance R was connected in series with glass sample.

Theory

The DC conductivity of semiconducting oxide glasses for the hopping of polarons in a non adiabatics approximation is given by Austin *et al*. (1969) and Mott (1968).

$$\sigma = ne\mu$$

$$= (v_0Ne^2R^2/kT)\ C(1-C)\ \exp(-2\alpha R)\ \exp(-W/kT)$$

$$C(1-C)\ \exp(-2uR)\ \exp(-W/kT) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (1)$$

Where n is the number of metal ion sites per unit volume and C is the ratio of ion concentration in low valance state to total concentration of metal ions; the exp (2αR) represents the electron overlap integral between sites, R is the hopping distance and W is activation energy.

Assuming that a strong electron lattice interaction exists, the activation energy W is the results of polaron formation with binding energy W_p and any energy difference W_D which might exists between the initials and final sites due to variations of the local arragments of ions. Austion and Moth (1969) have shown that.

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

$$= W_D \quad \text{for } T > \theta_D/2 \ldots\ldots\ldots\ldots (3)$$

Where W is the polaron hopping energy, W_H is the disorder energy arising from the energy difference between two neighboring hopping sites and θ_D is Debye temperature. The polaron hopping energy W_H is given by.

$$W_H = W_p / 2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Where W_p is the polaron binding energy. The polaron hopping energy W_H calculated from the theory by Austin and Mott (1969) is

$$W_H = e^2/4\varepsilon_p (1/r_p - 1/R) \ldots\ldots\ldots\ldots (5)$$

Where,

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

Where ε_3 and ε are the static and high- frequency dielectric constants of the glass respectively, ε_3 epis the effective dielectric constants (Bogomolov *et al*., 1967) r_p is the polaron radius estimated from the site spacing R (for crystal like solids). According to Bogomolov *et al*. (1968)

$$r = (1/2)(\pi/6N)^{1/3} = (R/2)(\pi/6)^{1/3} \ldots\ldots\ldots\ldots (7)$$

Two methods have been suggested to calculate the polaron binding energy. Most general expression is given by Hostein, (1959).

$$W_P = \frac{1}{2n} \sum_q \left| V_q \right|^2 h\acute{\omega}_q$$

Where Vj is the electron-photon coupling constant, o(. is the frequency of optical photons of wave numbers q and N is the site density.

Another methods has been given by Mott, (1969) which gives a direct estimate (for polar lattices, if the distance R through which the electron must be transferred is not large compared to r)

$$W_p = \tfrac{1}{2} (e^2 / \epsilon_p r_p) \ldots\ldots\ldots\ldots (9)$$

In a generalized polaron model, the activation energy is

$$W = W_H - J \ldots\ldots\ldots\ldots (10)$$

Where J is polaron band width which is related to the electron wave function overlap on adjacent sites. The nature of the hopping conduction mechanism (adiabatic or non adiabatic) following methods have been suggested.

1. Friedman and Holstein, (1963) derived an expression for the mobility in the case non-adiabatic hopping;

$$\mu = 3/2(eJ^2R^2/kT)(\pi/kTW_H)^{1/2}\exp(W/kT) \ldots (11)$$

While Emin and Holstein, (1969) derived an expression for the mobility inthe case of adiabatic hopping.

$$\mu = \frac{4}{3} \left(\frac{e\, \acute{\omega}_o R^2}{kT} \right) \mathrm{Exp}[(J - W_H)/kT] \ldots (12)$$

2. In the second method, the polaron band width J should satisfy the inequality suggested by Holstein (1959).

$$J > \left(\frac{2kTW_H}{\pi} \right)^{1/4} \left(\frac{h\,\acute{\omega}}{\pi} \right)^{1/2} \ldots (13)$$

Adiabatic hopping

J < J* Non adiabatic hopping

The polaron band width J can beestimated from

$$J \approx e^2 \{N(E_F)\}^{1/2} \epsilon_p^{1/2} \ldots\ldots\ldots\ldots (15)$$

Where $N(E_F)$ is the density of states at the Fermi level J can be estimated from equation 15.

Recently Triberies and Friedman 1985; Triberies, 1985 have applied percolation theory to the small polaron hopping regime and evaluated the conductivity in the disordered system considering co-relation due to energy of common sites in the percoloation cluster, the

following expression for the conductivity has been obtained.

$$\sigma = \sigma_o \exp [-(T_o/T)^{1/4}] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(16)$$

Where σ_0 and T are constants and T_0 is given by

$$T_o = 19.44\ \alpha^3 /kN\ (E_F) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(19)$$

Where N(E) is the density of state Fermi level.

RESULTS AND DISCUSSION

The dc electrical conductivity of the glasses of $V_2\ O_5$- $B_2\ O_3$ is measured in the temperature range 303 to 523 K. The conductivity is calculated by measuring the dc resistance of the samples at different temperature. It is observed that the resistance of the sample depends on temperature and follows the Arrhenius equation over a certain temperature range. The variation of conductivity with temperature for various composition of V, (____) is shown in Fig. 3/ From the plot it is observed that the conductivity variation is non linear and conductivity increases linearly at somewhat high temperature region and the rate is slow at low temperature region. The conductivity of these glasses varies from 10^{-5} to 10^{-11} (ohm cm)' Which is in quite agreement with the values reported by Singh *et al*. (1988) the dc Conductivity is $V_2\ O_5$ composition dependent and it is observed to be maximum for 20 mol% of $V_2\ O_5$ at 473K. All the glass samples studied indicate a negative temperature coefficient and a predominate electronic conduction which occurs due to polarons. Ft is observed that the log a versus 1/t plots are not linear, indicating temperature dependant activation energy which is the characteristics of small polaron hopping conduction (Austin *et al*., 1969; Mott, 1968; Holstein, 1959; chung *et al*., 1979; ghosh and chakravarty, 1991). The value of polaron radius r is evaluated by using the eq. (7). This value is found to be of the order of 1.6 A^0 which is expected for small polaron because of the non-linear behavior of log a versus I IT plot the activation energies are evaluated at (473 K) and are plotted in fig. 3. It is seen that the activation energy is temperature and composition dependent. The value of activation energies are found to be in the range of 0.013 to 0.04eV. The activation energy is higher for 5 mol% and lower for 20 mol% of $V_2\ O_5$ at temperature 473 K. The value of activation energies are found tobe of the order of vanadate glasses (Yawale and Pakade, 1993); mott nd davis, 1979). Polaron binding energy W is calculated from the theory [eq. (9)] of Austin *et al*. (1969). The value of effective dielectric coasiani is calculated by considering the high frequency dielectric constant e» from the Debye semicircle. Using this value hopping energy W is calculated. These values reported in table 1.

Considering V^{5+} as donors and V^5 acceptors, the electron conduction though polaron and ?or hopping necessitates the simultaneous presence of both sites and due to expotencial decrease in the radial wave finction, conduction increase as these sites come neare. The site symmetry of V^5 ions in glass matrix is identical to that of V^5 ions and the conduction of the glass. Thus the electronic conduction process through mixed valences according to the

$$V^{4+} \_O\_ V^{5+} \rightarrow V^{5+} \text{ -- } O\text{—}V^{4+}$$

The nature of hopping conduction (adiabatic OR non-adiabatic) is examined by the condition given by Holstein , (1959). According to Holstein the polaron band width J should satisfy the inequality of equaltion (J J*). Accordingly the values of J and J* are calculated and reported in tables 1. The value of J for the glass samples studied are found to be less than j* suggesting that the nature of hopping conduction is non adiabatic.

Table 1: transport properties of vanadium borate glasses.

Mol of V_2O_3	Glass sample	Polaron binding energy (W_p) eV	Polaron hopping energy (W_H) eV	Polaron band width J eV	J* eV,	Effective dielectric constant (ε_p)	Localization length (α) A^0	Density *of* states at Fermi level $N(E_F)\ 10_{19}$ $eV^1cm^{\ 3}$	Density of Localized states N_0 $10^{19}eV^1cm^3$
5	VB1	0.014	0.007	0.043	0.055	169	4.06	0.53	1.15
10	VB2	0.025	0.013	0.036	0.063	108	7.29	3.95	0.15
15	VB3	0.031	0.016	0.019	0.067	81	3.76	0.36	1.69
20	VB4	0.022	0.011	0.043	0.061	111	1.61	0.48	1.42
25	VB5	0.034	0.017	0.023	0.068	80	4.61	0.92	0.66

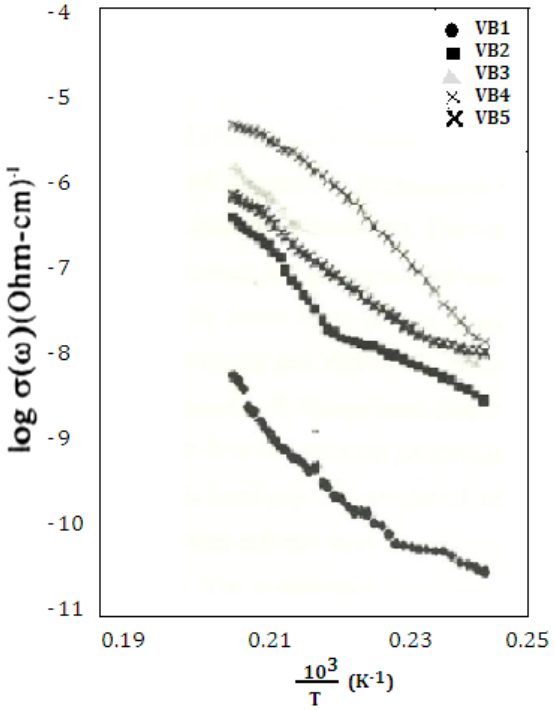

Fig.1: Plot of variation of dc conductivity with temperature for Vanadium- Borate glasses.

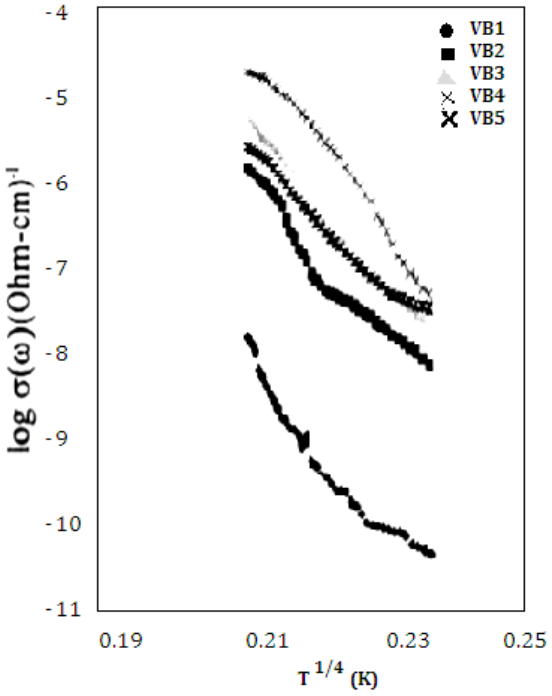

Fig.2: Plot of variation of dc conductivity with temperature (Mott $T^{-1/4}$ analysis) for Vanadium-Borate glasses

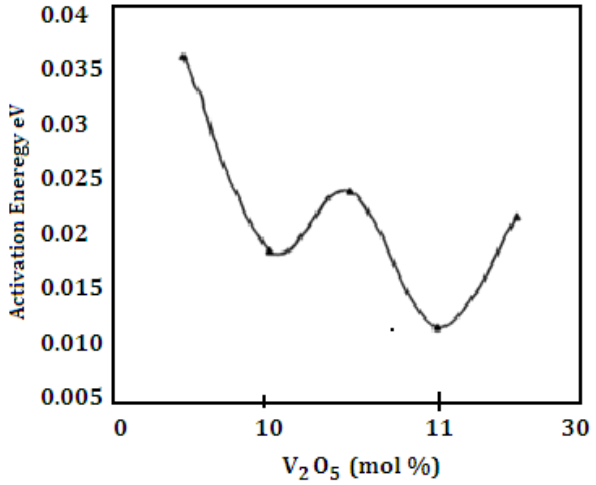

Fig. 3 : Plot of activation energies evaluated at 473K temperature versus V_2O_5 mol%

The conductivity (Mott, 1969) for the variable hopping range is given by eq. (18) form which the plot of log 0 against T^1 is drawn (Fig. 2). The slope of the plot gives T_0 value which yields the value of density of states at Fermi level N (E_K). The value of N (E_F) are reported in table 1.

Triberies and Friedman (1985) have appied the percolation theory to the small polaron hopping regime and evaluated the conductivity in the disordered systems. The correlation due to the energy common sites in the percolation cluster is considered and the expression for the conductivity is evaluated. The same plot of log a versus T^{UA} (Fig. 2) is used and from, the slope, the values of localized states (N_0)are evaluated (Table 1). It is cleasr that the plot (fig.2) is linear over a small temperature region and the values of a, NT and N(E_0) obtained are found to be reasonable for localized states.

CONCLUSION

In general it is concluded that the non adiabatic hopping conduction is observed in V_2O_5 -B_2O_3 glasses. The small polaron model is applicable. The percolation model suggested by Tiberius and Fridman (1985) and Mott's $T^{",/4}$ (Mott, 1969) interprets states are found to be reasonable.

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