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Electrical conduction in some vanadate glasses

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The preparation of two series of BaO–V_2O_5 and V_2O_5–B_2O_3 glasses and their results for electrical conductivity, density and molar volume are reported. Conduction in the BaO–V_2O_5 glass system is electronic. Trapping levels are involved in the transport process and the conduction is believed to be due to hopping of carriers between localized states. Density and molar volume data suggest a compact structure of these glasses.

1. Introduction

The fundamental problem of conduction in amorphous materials is how the electron energy spectrum, the character of the energy states and the transition probability between the states are changed in going from the crystalline to the amorphous phase. Much attention has been given to this problem by experimental as well as by theoretical physicists and they believe that understanding the nature and distribution in energy of the localized states is perhaps most important because the presence of a high density of localized states makes it necessary to consider direct hopping of carriers between traps (localized states) as a probable mechanism of transport [1, 2].

The electronic conduction in oxide glasses is primarily due to the presence of transition metal ions of different valencies in the glass [3]. Conductivity arises through electron transfer from a lower to higher valence state, e.g. (V^{4+} to V^{5+}). The mechanism is considered to be analogous to that postulated for transition metal oxides.

In the present work an attempt has been made to explain density, molar volume and particularly the conduction mechanism in the glasses under investigation as part of an attempt to solve the complex problem of understanding the nature of electronic processes in transition metal oxide materials.

2. Experimental work

2.1. Glass preparation

Two different series of glasses BaO–V_2O_5 and V_2O_5–B_2O_3 were prepared by using analytical reagent grades of BaO, V_2O_5 and B_2O_3 in which the B_2O_3 was 99.999% pure. Both series of glasses were prepared by the standard method of sudden cooling from 900° C of a melt contained in a platinum crucible. After casting, the 3 mm thick glasses were annealed at 200° C for 3 h to relieve the mechanical stresses and to prevent cracking.

2.2. X-ray and density measurements

In order to test the crystallinity of a glass the X-ray diffraction pattern is usually obtained by allowing a finely collimated X-ray beam to fall upon the sample and by recording the scattered radiation upon a film surrounding the material. The present experiment was carried out with a Debye–Scherrer powder camera and the diffraction patterns showed no sharp rings but only diffuse haloes, a behaviour which is characteristic of glassy materials. The densities of the annealed glasses were determined at room temperature by the general Archimedes displacement method using toluene as an immersion liquid.

2.2.1. Results and discussion

The densities of all the glass samples along with the derived molar volumes are listed in Table I. Figs. 1 and 2 represent the density and molar volumes of BaO–V_2O_5 glasses as a function of composition. The curve of the density data (Fig. 1) leads to a value from 3.44_3 to 3.74_4 as the BaO content increases from 20 to 40 mol%. The molar volume clearly decreased as the density of glasses increased with increasing BaO content (Fig. 2). Drake *et al.* [4] proposed that the mono-

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TABLE I Densityand molar volume of some vanadate glasses

Specimen	BaO content (mol %)	V_2O_5 content (mol %)	B_2O_3 content (mol %)	Relative density	Molar volume
k	20	80	–	3.44_3	51.1_5
l	25	75	–	3.56_1	49.0_5
m	30	70	–	3.64_4	47.5_5
n	35	65	–	3.71_5	46.2_5
o	40	60	–	3.74_4	45.5_1
f	–	5	95	1.97_9	37.9_9
g	–	10	90	2.08_5	38.7_5

tonic change of molar volume with composition suggests that the structure of glass does not change. Fig. 2 signifies that the molar volume changes monotonically and there is no significant change in the structure of the glass. The linear variation of density as plotted against the composition of the modifying oxide is in good agreement with the results of Shartsis and Shermer [5] as given in Fig. 1 and show an increased rigidity in the structure of glass as the BaO content increases, as described by Hogarth and Ghauri [6] for another system of phosphate glasses.

2.3. Electrical conductivity measurements

The electrical circuit used for the d.c. conductivity measurements was composed of a Keithley 610 C electrometer, a high voltage power supply and a specially designed specimen holder with heating unit. Gold electrodes including guard rings were deposited on to 2 mm thick polished glass samples by vacuum evaporation. All the measurements were made under a vacuum of $\sim 10^{-5}$ torr to avoid certain atmospheric effects.

2.3.1. Results

Table II shows the conductivity results for the glasses examined. The d.c. conductivity (σ) increases with temperature and also with increase in the concentration of the transition metal oxide in the glass as shown in Figs. 3 and 4. All glasses show a smooth variation of conductivity with $10^3/T$. The activation energies were calculated from the slopes of the $\log \sigma$ against $1/T$ curves and found to decrease as the concentration of transition metal oxide was increased in the glass. The conductivity of barium–vanadate glasses was found to be much higher than that of the

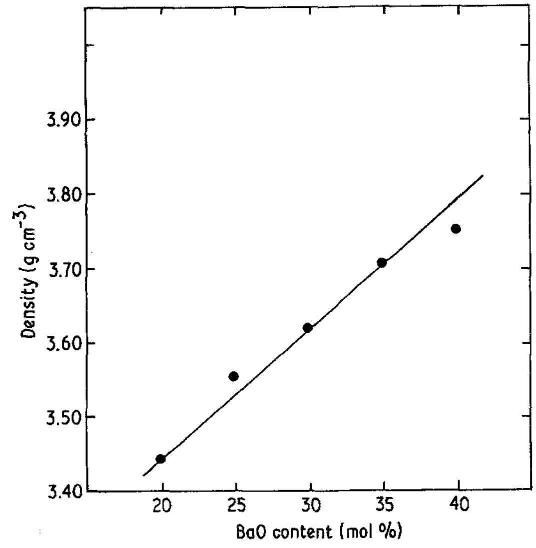

Figure 1 Density of barium–vanadate glasses as a function of composition.

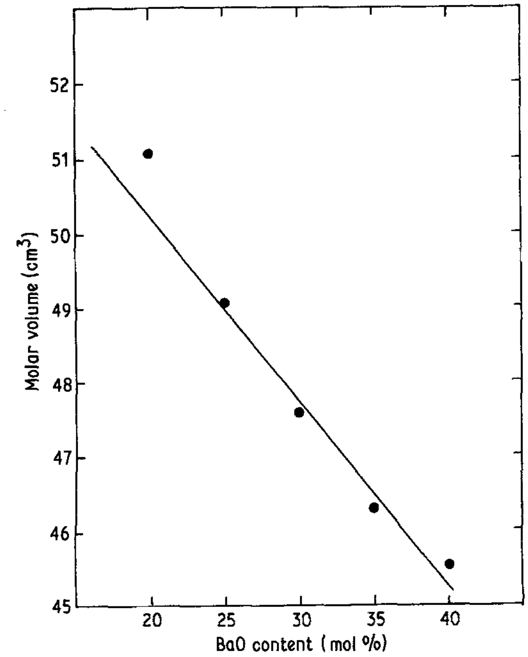

Figure 2 Molar volume of barium–vanadate glasses as a function of composition.

TABLE II Physical parameters of some vanadate glasses

Specimen	$N \times 10^{-21}$ (cm^{-3})	V–V spacing (nm)	Polaron radius, r_p (nm)	Activation energy, W (eV)	$-\log_{10} \sigma$ at 100° C (σ in ohm^{-1} cm^{-1})
k	9.31	0.475	0.191	–	–
l	9.20	0.477	0.192	–	–
m	8.86	0.483	0.194	0.34	4.25
n	8.46	0.490	0.197	0.40	5.53
o	7.91	0.501	0.202	0.54	6.42
f	0.87	1.00	0.422	0.57	10.42
g	1.55	0.864	0.348	0.49	9.14

corresponding vanadium–borate glasses. Fig. 5 shows the variation of high temperature activation energy W with concentration. It is clear that by increasing the V_2O_5 content the activation energy decreases. A general trend observed in Fig. 6 is that the magnitude of the conductivity at any temperature tends to be smaller in those glasses having the highest thermal activation energy. This agrees with the results published by Sayer and Mansingh [7] and by Chung and Mackenzie [8]. Fig. 7 shows curves of $\log \sigma$ at 100° C as a function of V_2O_5 concentration and it is seen that as the concentration of V_2O_5 oxide increases the conductivity also increases. The value of the pre-exponential factor σ_0 was found to be almost constant.

In order to check the type of conduction in the present series, the resistance of all glasses was measured as a function of time. The fixed voltage of 300 volts for V_2O_5–B_2O_3 glasses and 30 volts for BaO–V_2O_5 glasses was applied over an extended period of time and resistance was measured continuously. The graphic representation of the results of this experiment is shown in Figs. 8 and 9. The resistance of BaO–V_2O_5 glasses is independent of time (Fig. 8). This may be taken as evidence that the polarization effect in these glasses is absent and the electrical conductivity would in this case be due to transport of electrons rather than ions. In the V_2O_5–B_2O_3 glasses, apart from the short term initial variation with time the current is essentially constant.

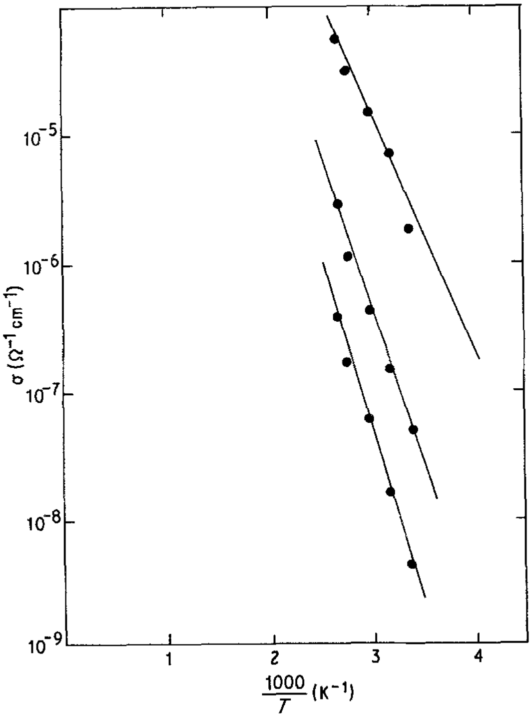

Figure 3 Conductivity against inverse temperature for BaO–V_2O_5 glasses.

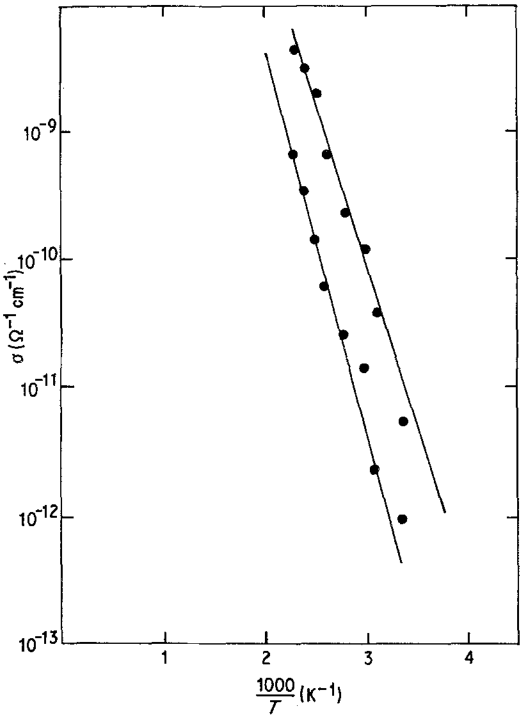

Figure 4 Conductivity against inverse temperature for V_2O_5–B_2O_3 glasses.

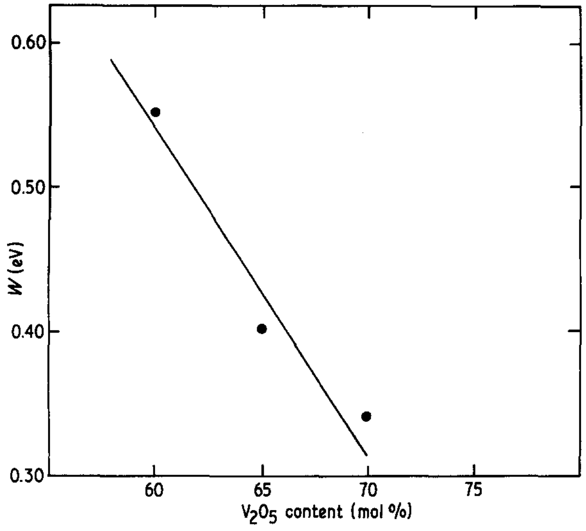

Figure 5 Activation energy of BaO–V_2O_5 glasses as a function of V_2O_5 content.

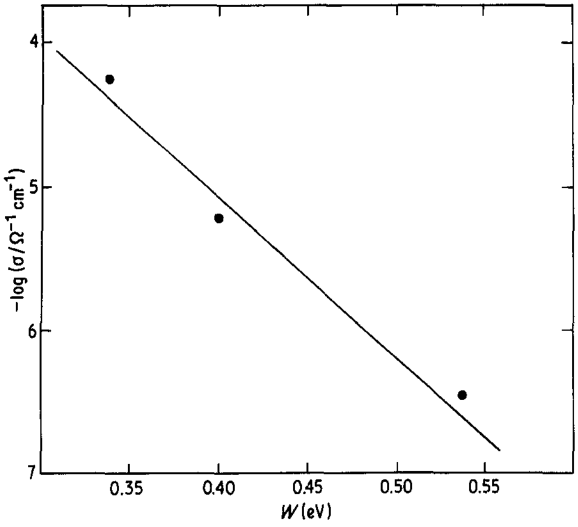

Figure 6 Logarithmic plot of conductivity against high temperature activation energy for BaO–V_2O_5 glasses. Conductivity values measured at 100° C.

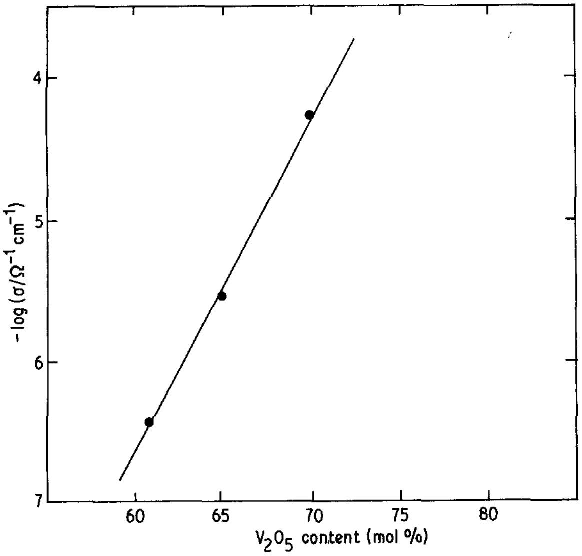

Figure 7 Logarithmic plot of conductivity against V_2O_5 content for BaO–V_2O_5 glasses. Conductivity values measured at 100° C.

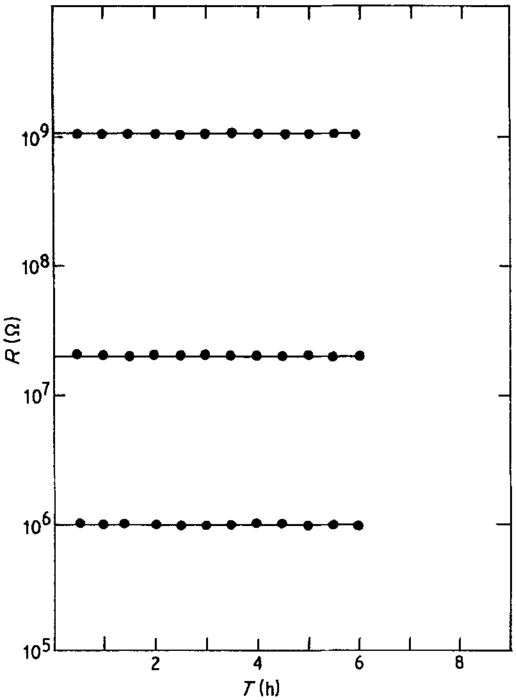

Figure 8 Resistance against time for $BaO–V_2O_5$ glasses.

The average V–V spacing was determined by using the total ion concentration in the formula

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

where N can be determined as described by Nester and Kingery [9]. Fig. 10 represents the activation energies as a function of V–V spacing. The variation of ion spacing with concentration is shown in Fig. 11.

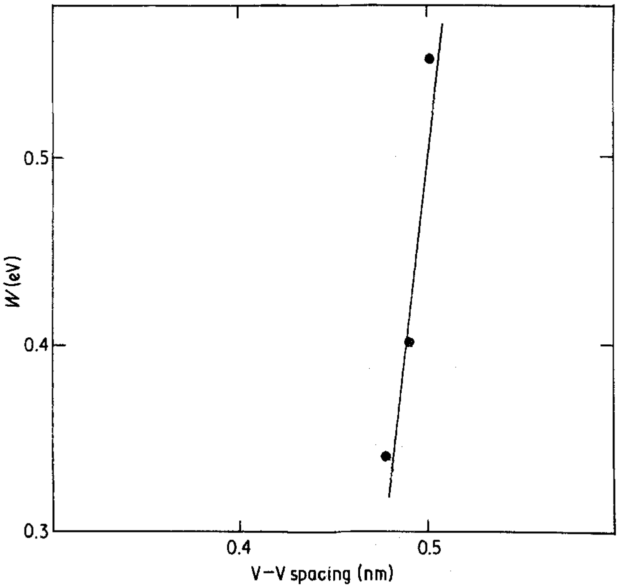

Figure 10 Activation energy as a function of V–V spacing.

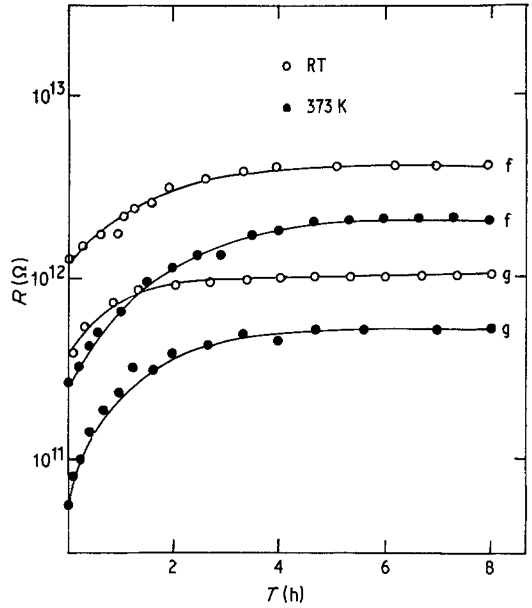

Figure 9 Resistance against time for $V_2O_5–B_2O_3$ glasses.

2.3.2. Discussion

The d.c. electrical conductivity of the glasses under consideration was found to be mainly dependent on the transition metal oxide. It is generally recognised that transition metal oxide exhibits semiconductivity and the conduction in such glasses is due to a hopping process, that is the transfer of an electron between the ions of the same metal in different valence state [3], e.g. $V^{4+} \rightarrow V^{5+}$. The pre-exponential factor in the present glasses was found to be almost constant while on the other hand the conductivity was a

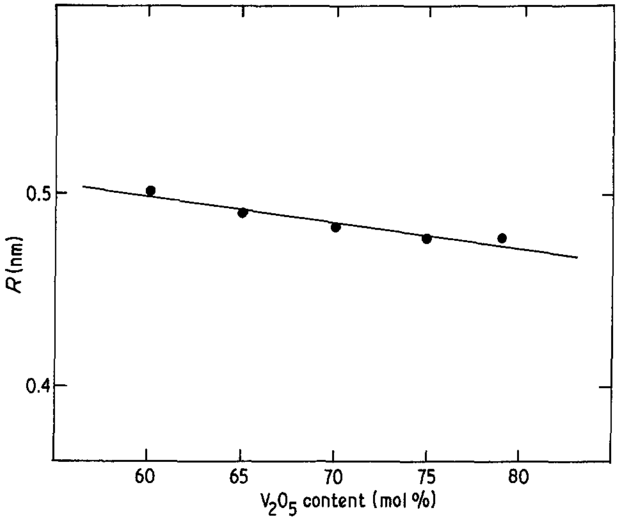

Figure 11 V–V spacing as a function of V_2O_5 content.

function of transition metal oxide content. The change in composition mainly affects the activation energy (Fig. 5). In fact an increase in a transition metal oxide content results in a decreasing transition metal ion spacing (Fig. 11) which accordingly leads to a decrease in the activation energy W (Fig. 10). The small polaron radius r_p was calculated from the relation $r_p = (1/2)(\pi/6N)^{1/3}$ postulated by Bogomolov *et al.* [10].

According to the small polaron theory, r_p should be smaller than the site separation and greater than the radius of the ion on which the electron is localized. The r_p values obtained here are recorded in Table II. The polaron radius is a function of transition metal oxide in these glasses and decreases as the tranistion metal oxide content increases. Table II shows that r_p for each composition is less than the site spacing. Generally the conduction mechanism in the glasses under investigation could be summarized as follows:

(i) The conduction in these glasses at low field is ohmic.

(ii) The log conductivity against reciprocal temperature plots display behaviour which is typical of a small polaron hopping mechanism exhibited by 3d and 4d transition metal oxide glasses [11].

(iii) The transition metal oxide is the dominant component in these glasses.

(iv) The activation energy decreases and conductivity increases with increasing transition metal oxide concentration.

(v) The pre-exponential factor is almost constant.

(vi) The conduction mechanism in $BaO–V_2O_5$ glasses in the glass formation range is certainly electronic but the $V_2O_5–B_2O_3$ glass system may be a mixed electronic/ionic conductor [12].

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