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Non-linear concentration-dependent electrical properties of some semiconducting vanadate glasses

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Characterizations of (50 − x) P_2O_5–xM–50V_2O_5 (M = Bi_2O_3, Sb_2O_3, and GeO_2 and $x = 0$ to 45 mol% M) and P_2O_5–Bi_2O_3 semiconducting oxide glasses have been made from studies of electrical conductivities (both a.c. and d.c.) in the temperature range 77 to 400 K. All these glasses showed some interesting non-linear variation of d.c. and a.c. conductivity, together with other properties for particular values of M (between 20 and 30 mol% M). Because the non-vanadate (1 − x) P_2O_5–x Bi_2O_3 glasses also showed similar conductivity anomaly (minimum) around 25 mol% Bi_2O_3 with a corresponding maximum in the activation energy (W), it is concluded (in contradiction to earlier suggestions) that not only the ratio β (= V^{5+}/V^{4+}) but also the network-former ions in the vanadate glasses make a substantial contribution to the anomalous concentration variation of the physical properties of these glasses. The electrical conduction in these glasses is found to be mainly due to hopping of polarons in the adiabatic approximation. At low temperature, the d.c. conductivity obeys Mott's $T^{-1/4}$ behaviour. The a.c. conductivity obeying the general ω^s law (exponent s lying between 0.85 and 0.98) supports the theory based on the hopping over the barrier model.

1. Introduction

It is well known that the semiconducting oxide glasses (SOG) with transition metal ions (TMI) have very interesting electrical and other properties [1–20]. Some of these glasses also have very important technological applications [3, 4]. Among the various oxide glasses with transition metals such as copper, vanadium, iron, etc., the physical properties of the vanadate glasses have been most extensively studied [5–19]. The thermal variations of the electrical properties of most of these glasses are almost the same [5–19]. But these properties of the SOG, when carefully studied as a function of concentrations (either the TMI or the glass-forming oxides) at a constant temperature, do not always show a linear behaviour [5–8]. Earlier, Rao [7, 8] first showed the anomalous variation of the ratio (V^{5+}/V^{4+}) in the V_2O_5–P_2O_5–GeO_2 glasses which, in turn, caused non-linear variation of conductivity and magnetic properties of these glasses. However, no systematic investigation of the anomalous behaviour from the studies of various physical properties of these glasses over a wide range of concentrations has so far been made. Furthermore, this anomaly in the electrical conductivity was attributed [5, 6] solely to the anomalous variation of the ratio $\beta = (V^{5+}/V^{4+})$. This contention appears to be not strictly valid. The anomalies in the electrical conductivity or in other properties might also be related to the characteristic features of the glass-forming oxide (GeO_2, Bi_2O_3, etc). The non-transition metal oxide glasses might even show similar types of anomalies in the physical properties, as mentioned above.

In the present paper the experimental electrical conductivity data of two series of oxide glasses, namely vanadate 50 V_2O_5–(50 − x)P_2O_5–xM (M = Bi_2O_3, Sb_2O_3, and GeO_2, VPB, VPA and VPG, respectively) and the non-vanadate P_2O_5–Bi_2O_3 (PB) glasses, are analysed. The behaviour of the concentration-dependent magnetic properties is discussed in the following paper [19]. Although both the vanadate (VPB, VPA, and VPG) and the non-vanadate (PB) glasses show interesting anomalous properties, the origin of the anomalies are not the same as discussed in this paper. It was earlier concluded [5, 6] that in the vanadate glasses the anomalous variation of β (= V^{5+}/V^{4+}) with concentration is only responsible for showing conductivity minima. To show that even the non-vanadate glasses show these minima in the concentration-dependent conductivity curve, we have studied the electrical and other properties of the P_2O_5–Bi_2O_3 glass with different concentrations of Bi_2O_3.

2. Experimental procedure

The VPB, VPA and VPG glasses were prepared following the procedure of our earlier work [9, 10, 20] by a quick quenching technique. Very good stable and homogeneous glass with metallic lustre was obtained

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TABLE I Some parameters of the VPA, VPB, VPG, and PB glasses

Glass number	V_2O_5 (mol %)	P_2O_5 (mol %)	Bi_2O_3 (mol %)	Sb_2O_3 (mol %)	GeO_2 (mol %)	Conc. V^{4+} (10^{21} cm^{-3})	β ($= V^{5+}/V^{4+}$)
(VP)	50 (49.31)[a]	50	0	0	0	3.90	1.56
(VPB1)	50 (48.99)	35	15	0	0	3.30	2.33
(VPB2)	50 (49.02)	25	25	0	0	4.32	1.78
(VPB3)	50 (49.08)	10	40	0	0	3.22	2.57
(VPA1)	50 (48.90)	35	0	15	0	5.20	1.32
(VPA2)	50 (49.10)	25	0	25	0	5.49	1.13
(VPA3)	50 (49.08)	10	0	40	0	4.60	1.44
(VPG1)	50 (49.10)	35	0	0	15	4.98	1.54
(VPG2)	50 (49.21)	25	0	0	25	5.20	1.44
(VPG3)	50 (48.90)	10	0	0	40	4.51	1.54
(PB1)	0	90	10	0	0	–	–
(PB2)	0	80	20	0	0	–	–
(PB3)	0	75	25	0	0	–	–
(PB4)	0	60	40	0	0	–	–

[a] The values within the parentheses correspond to the values obtained from chemical analysis.

for each of the glasses. Similar procedure was also followed to prepare the PB glasses. The amorphous nature of all the glasses was checked by X-ray diffraction (Philips, PW-1050/51 model) and also by scanning electron micrographic (SEM, Hitachi, Japan) studies as reported earlier [5, 6]. The glass transition temperatures, T_g, of the glasses (measured with a Shimadzu DT-30 thermal analyser with a heating rate of 20 °C min^{-1}) showed non-linearity around 20 to 25 mol % M [5, 6]. Similarly the variation in densities of the glasses with concentration also showed [5, 6] an anomalous variation at approximately the same concentration at which T_g showed a non-linearity.

Following the procedure of our earlier work [9, 10] the concentrations of the V^{4+} and V^{5+} ions were estimated chemically and are shown in Table I. It has, however, not been possible to estimate the concentrations of the V^{3+} and V^{2+} ions which might also be present in the vanadate glasses.

2.1. Electrical measurements

The detailed method of measurements of d.c. and a.c. conductivities of the prepared glasses has already been discussed [9, 10, 20]. The temperature-dependent d.c. conductivity was measured with a Keithley 640b Vibrating Capacitor Electrometer. The a.c. conductivity ($\sigma_{a.c.}(\omega)$) measurements were made using a General Radio (Model 1615A) capacitance bridge which measures equivalent parallel conductance and capacitance of a sample for frequencies between 20 and 10^5 Hz in a three-terminal arrangement. These measurements were made in the temperature range 77 to 450 K with a stability of ± 0.5 K (or better).

3. Results and discussion

3.1. D.c. conductivity

The logarithm of the d.c. conductivity of the VPB, VPA, and VPG glasses for various concentrations of Bi_2O_3, Sb_2O_3, and GeO_2 is shown in Fig. 1. It is observed from the curves that for all the fixed temperatures (200 K, 250 K and 300 K) the conductivity ($\sigma_{d.c.}$) of the VPB glasses is always higher than that of the pure base glass ($50V_2O_5$–$50P_2O_5$, VP glass). The value of $\sigma_{d.c.}$ increases with concentration of Bi_2O_3 in the VPB glass up to about 15 mol % and then $\sigma_{d.c.}$ decreases until a minimum around 20 to 25 mol % Bi_2O_3 is attained. With further increase of Bi_2O_3, ($\sigma_{d.c.}$) begins to increase up to the range beyond which no VPB glass is formed. On the other hand, the d.c. conductivity ($\sigma_{d.c.}$) of the VPA glasses is always lower than that of the VP glass, and $\sigma_{d.c.}$ decreases to a minimum value between 20 and 25 mol % Sb_2O_3 and then increases with further increase of Sb_2O_3 up to the range beyond which no glass is formed. For the VPG glasses variation of $\sigma_{d.c.}$ with GeO_2 concentration is almost similar to that of the VPA glass (Fig. 1). This behaviour of the present oxide glasses, also reflected in their physical properties, distinguishes them from that of many other TM oxide glasses [14].

It is quite interesting to mention that even for the PB glasses the concentration-dependent d.c. conductivity at each of the three different temperatures (200 K, 250 K and 300 K) shows (Fig. 2) a minimum around 20 to 30 mol % Bi_2O_3. An almost similar nature of the log $\sigma_{d.c.}$–Sb_2O_3 concentration curve was also noticed for the P_2O_5–Sb_2O_3 glasses [21]. Therefore, the anomalous variation of conductivity as a function of concentration observed in the vanadate glasses, is also

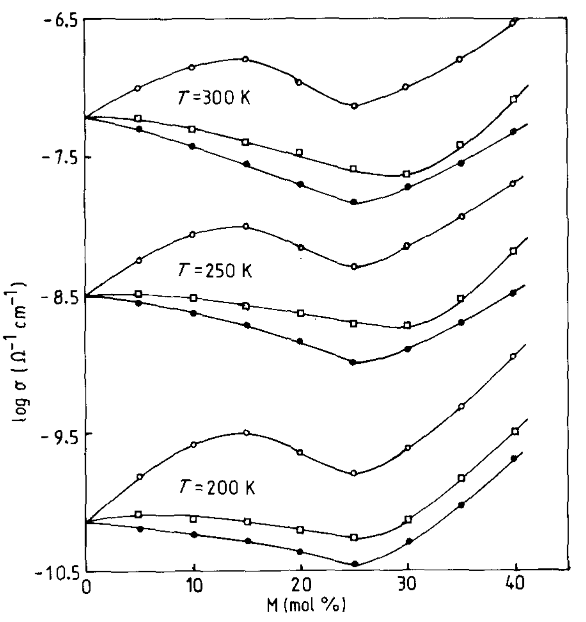

Figure 1 Variation of $\log \sigma_{d.c.}$ with concentration, x, of Bi_2O_3, Sb_2O_3, and GeO_2 at three fixed temperatures. (○) VPB, (☐) VPG, (●) VPA.

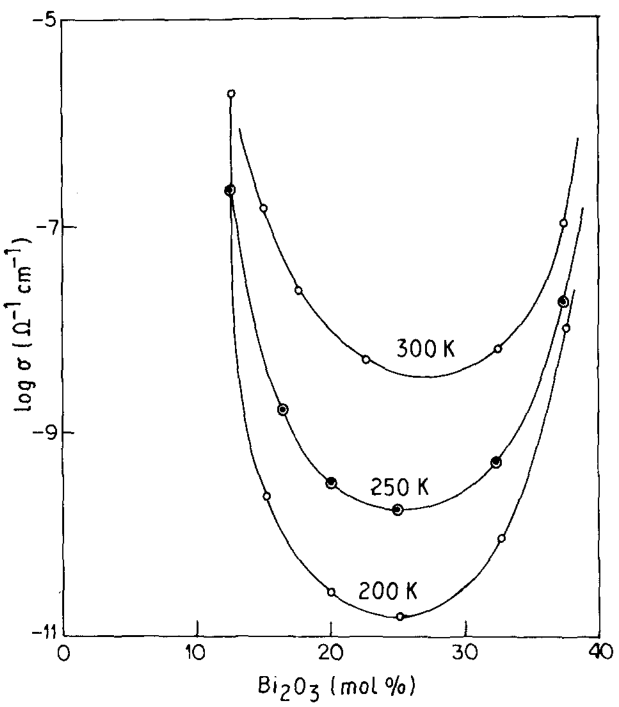

Figure 2 Variation of log $\sigma_{d.c.}$ of the P_2O_5–Bi_2O_3 (PB) glasses with concentration of Bi_2O_3 at three fixed temperatures.

observed in the d.c. conductivity behaviour of the non-vanadate PB glasses.

From the present experimental observation we find that the addition of Sb_2O_3, Bi_2O_3, and GeO_2 to the base glass alters the ratio β (for vanadate glasses) in different ways, as shown in Table I and also Fig. 3. The ratio β for the VPB glasses is always larger than that of the base glass VP so that $\sigma_{d.c.}$ for these glasses is higher than that of the VP glasses. On the other hand, the conductivity ($\sigma_{d.c.}$) of the VPA glass is always lower than that of the VP glass due to the smaller values of β for these glasses (Table I). Addition of GeO_2 to the VP glass (the VPG glass) also gives rise to a slightly lower conductivity compared to the base glass (VP) in the low concentration region. In the PB glasses the conductivity minimum might be attributable to the bismuth and phosphorus, i.e. the network-former ions have a real effect causing anomalous

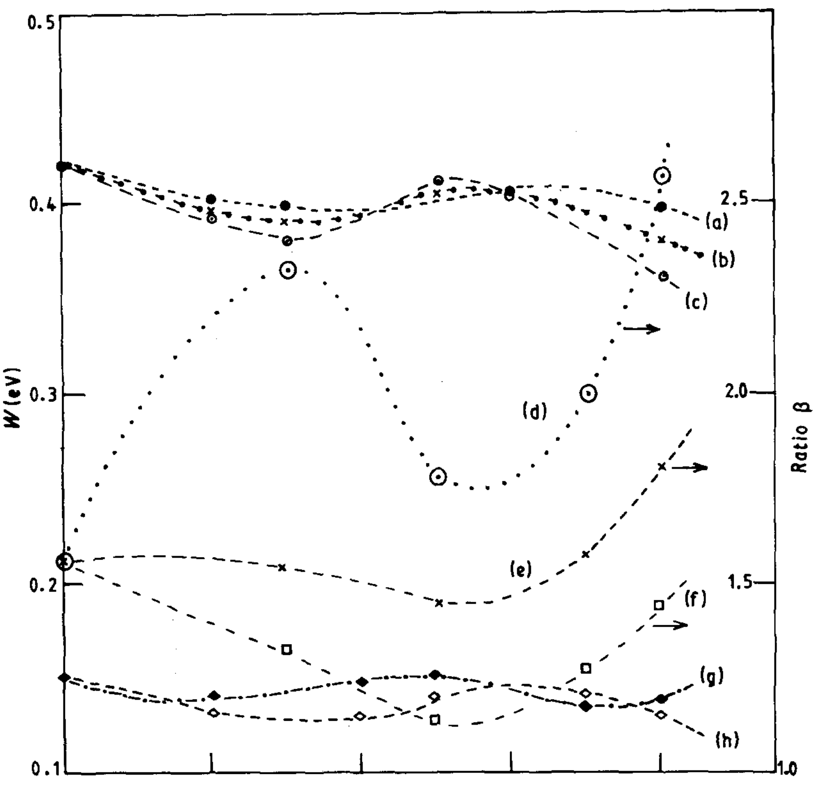

Figure 3 Variation of activation energy, W, and $\beta(=V^{5+}/V^{4+})$ of the VPA, VPG, and VPB glasses with concentration, x, of Sb_2O_3, GeO_2, and Bi_2O_3, respectively. (a, f, h) VPA, (b, d, g) VPB, (c, e) VPG, (a, b, c) 400 K and (g, h) 80 K.

TABLE II Different model parameters for the VPB, VPA, and VPG glasses

Glass number	Activation energy (eV) at		W_H (eV)	ΔW^a (eV)	r_p (nm)	R (nm)
	400 K	80 K				
(VP)	0.420	0.153	0.271	0.149	0.1870	0.4640
(VPB1)	0.382	0.141	0.282	0.100	0.1812	0.4490
(VPB2)	0.413	0.151	0.290	0.123	0.1760	0.4380
(VPB3)	0.363	0.133	0.280	0.083	0.1755	0.4432
(VPA1)	0.401	0.131	0.291	0.111	0.1770	0.4350
(VPA2)	0.400	0.132	0.280	0.120	0.1801	0.4402
(VPA3)	0.401	0.141	0.281	0.120	0.1760	0.4470
(VPG1)	0.385	0.135	0.290	0.095	0.1770	0.4230
(VPG2)	0.405	0.140	0.282	0.123	0.1770	0.4380
(VPG3)	0.381	0.142	0.284	0.097	0.1796	0.4365

$^a\Delta W = W$ at 400 K $- W_H$.

variation of electrical conductivity and other properties of these glasses. It is thus clear that the anomalous change of the ratio β is not the only reason for the presence of a conductivity minimum.

It is further observed that the present experimental results do not completely agree with those of Brown [18] who showed that a decrease of V^{4+} ions was associated with a decrease in conductivity. However, the present results support the findings of Rao [7, 8] that the decrease of V^{4+} ions gives rise to an increase of electrical conductivity.

Calculations of activation energy (W) from the slopes of Figs 4 and 5 as given in Table II show that above 200 K the activation energy of all the vanadate glasses is lower than that of the base glass (VP). The concentration, x, dependences of W for two fixed temperatures (400 and 80 K) as shown in Fig. 3 indicate that the increase of β corresponds to a decrease of W and hence an increase of conductivity (Fig. 3). The variation of W with Bi_2O_3 (mol %) for the PB glasses shows (Fig. 6) a hump around 20 to 25 mol % Bi_2O_3 corresponding to a conductivity minimum in that range of concentration (Fig. 2).

It is also seen from Fig. 3 that the activation energy, W, is directly related to the ratio β for the VPB, etc., glasses. The activation energy, W, shows a maximum value of 0.42 eV at 400 K for which the concentration of Bi_2O_3 is about 25 mol % (where β also shows a minimum). For the VPA and VPG glasses, on the other hand, the values of W are almost constant, 0.40 to 0.41 and 0.38 to 0.40 eV, respectively. At lower temperature (80 K), the activation energy is almost independent of temperature (Fig. 3) for all the VPA, VPB, and VPG glasses. For the VPA glasses (and also for the VPG glasses, not shown in the figure) W shows a minimum around 20 to 25 mol % Sb_2O_3/GeO_2, while for the VPB glasses there are both a maximum and minimum as in the case of electrical conductivity (Fig. 1). This behaviour distinguishes the VPB glasses from the VPA and VPG glasses studied here. This difference in the behaviour of VPB glass from that of the VPA or VPG glass may also be visualized from the density (ρ), and T_g variation as a function of concentration, which might be due to the differences in the glass structures of these systems [5, 6].

3.2. Theoretical discussion

An attempt was made to explain the d.c. conductivity of the VPA, VPB, and VPG glasses by considering the hopping of polarons in the nonadiabatic approximation [22, 23] and to fit the conductivity ($\sigma_{d.c.}$) data to the relation

$$\sigma_{d.c.} = \frac{\nu_{ph} e^2 A(1 - A)}{k_B T R_a} \times \exp(-2\alpha R_a) \exp(-W/k_B T) \quad (1)$$

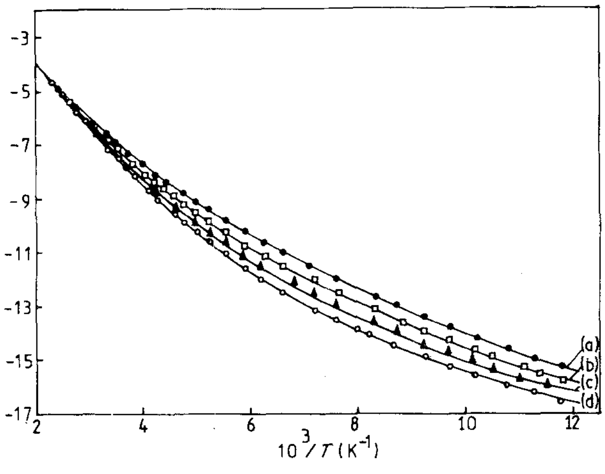

Figure 4 Thermal variation of d.c. conductivity of VPB glasses. Bi_2O_3 content: (a) 40 mol %, (b) 15 mol %, (c) 25 mol %, (d) 0 mol %.

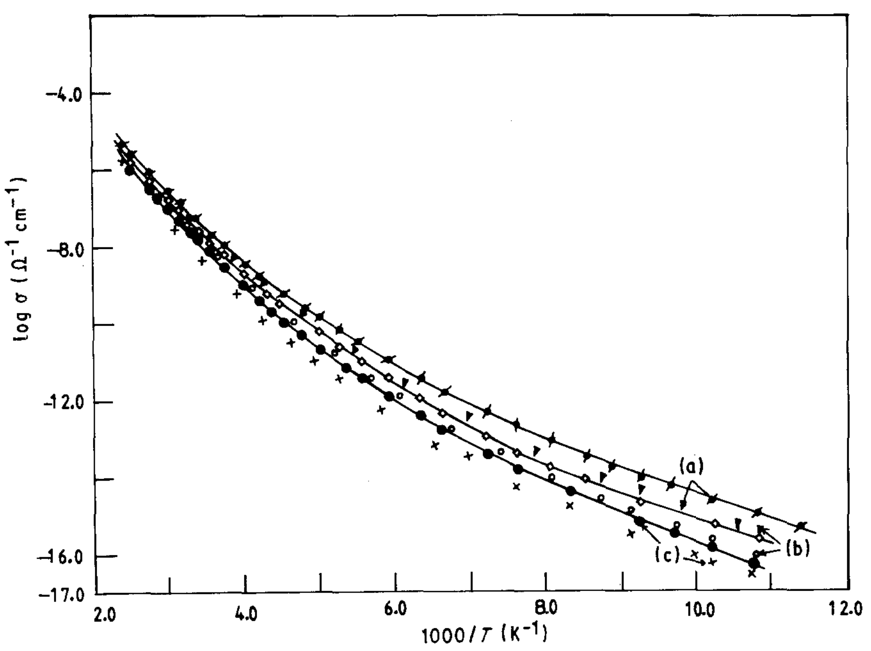

Figure 5 Thermal variation of d.c. conductivity of (⧫, □, ●) VPA, and (▼, ○, ×) VPG glasses. Sb_2O_3/GeO_2: (a) 40, (b) 15, (c) 25 mol %.

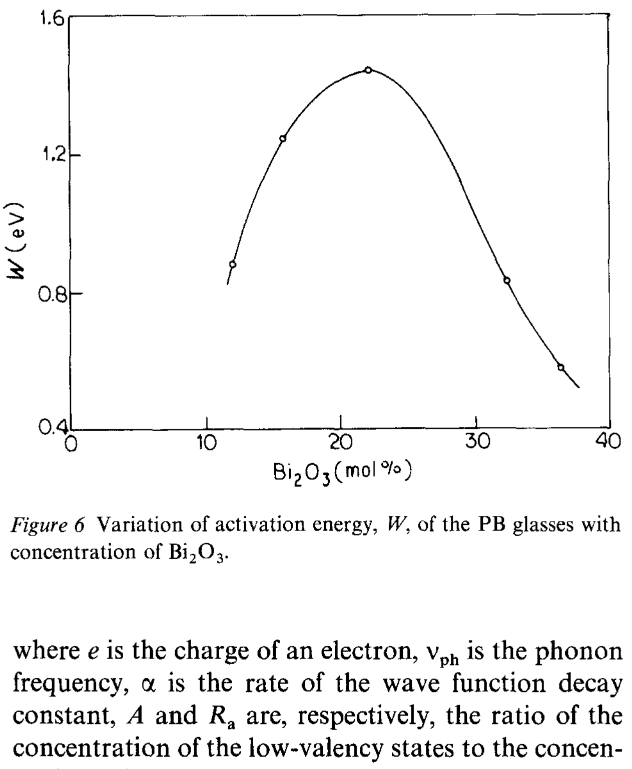

Figure 6 Variation of activation energy, W, of the PB glasses with concentration of Bi_2O_3.

where e is the charge of an electron, ν_{ph} is the phonon frequency, α is the rate of the wave function decay constant, A and R_a are, respectively, the ratio of the concentration of the low-valency states to the concentration of the total transition metal ions, and the average hopping distance, T and k_B are the absolute temperature and the Boltzmann constant, respectively. The activation energy W is given by

$$\begin{aligned} W &= W_H + W_D/2 \qquad T > \theta_D/2 \\ &= W_D \qquad\qquad\quad T < \theta_D/4 \end{aligned} \tag{2}$$

where W_H is the hopping energy, and W_D is the disorder energy, and θ_D is the Debye temperature given by $\theta_D = h\nu/k_B$.

The polaron radius, r_p, may also be estimated from the relation [24]

$$2r_p = (\Pi/6N)^{1/3} \tag{3}$$

where N is the total vanadium ion concentration. The estimated values of r_p (from Equation 3) are shown in Table II.

The polaron hopping energy, W_H, can also be calculated from the Austin and Mott's relation [22]

$$W_H = (e^2/4\varepsilon_p)\left(\frac{R - r_p}{r_p R}\right) \tag{4}$$

where $1/\varepsilon_p = 1/\varepsilon_\infty - 1/\varepsilon_0$, ε_0, and ε_∞ are the static and higher frequency dielectric constants, respectively. The calculated values of W_H from Equation 4 (assuming $\varepsilon_p = \varepsilon_\infty = n^2 = 4.30$, where n is the refractive index of the glass obtained from the reflectance spectra) are also shown in Table II.

An estimate of $W_D/2$ from the Miller and Abrahams' theory [25] gives $W_D = 0.10$ eV. Table II also shows that for the VPB type glasses the difference $\Delta W (= W - W_H)$ lying between 0.10 and 0.14 eV, is in general higher than the theoretically calculated values of $W_D/2$. A large deviation of ΔW values was also observed in the iron–phosphate glasses [26] and the discrepancy was attributed to the existence of two possible coordinations (4 and 6) for the iron ions. Such an argument seems to be not appropriate for the vanadate glasses because no different coordination has been found in the vanadate glasses studied so far [14].

The observed discrepancy in the activation energy obtained from the experiment and theory might be due to several reasons, namely, the different character of the glass-forming oxides (Bi_2O_3, Sb_2O_3, GeO_2, etc.) and/or values of A (Equation 1). Furthermore, the percentage of the ionic character of the respective cation–oxygen bonds (Sb–O, Bi–O, Ge–O, etc.) [27] is also different. With increasing Bi_2O_3 etc. contents, the ionic character changes non-linearly which shows a non-linear variation of the V^{5+}/V^{4+} ratio and hence the electrical properties. Because the change in the activation energy, W, due to the change in the A values (Equation 1) is very small [13, 14] the glass-forming oxides would be the dominant factor affecting the activation energy for hopping conduction in the present glass system.

3.3. A.c. conductivity

The values of log $\sigma_{a.c.}$–$10^3/T$ at difference frequencies ($f = \omega/2\Pi$) are shown in Fig. 7 for the VPA and VPG glasses with 25 mol % Sb_2O_3 and GeO_2. It should be noted here that the general behaviour of the $\sigma_{a.c.}$–T curves is similar to that reported for the TM oxide glasses [28]. A similar behaviour has also been observed [5, 6] for the other compositions of the VPA and VPG glasses, as well as for the VPB glasses.

In Fig. 8 log $\sigma_{a.c.}$ values of all three glasses are presented as a function of concentration, x, of M at 300 K. The $\sigma_{a.c.}$ values are found to decrease for all three glasses with increasing x, and $\sigma_{a.c.}$ for these glasses is always lower than that of the VP glass. However, an interesting point is that two separate rates of variation of $\sigma_{a.c.}$ values with x are seen; the first lies above 20 to 25 mol % M and the second below this concentration (see also Fig. 8). This behaviour definitely resembled the behaviour of d.c. conductivity, $T_g(x)$, and density $\rho(x)$. The frequency dependences of $\sigma_{a.c.}(\omega)$ for all the glasses (VPB, VPA, and VPG) are found to obey the general equation

$$\sigma_{a.c.}(\omega) = A\omega^s \qquad (5)$$

where A and s are the parameters to be calculated from the best fitting with experimental data ($\sigma_{a.c.}$). The values of s estimated from the slope of a.c. conductivity-frequency curves (Fig. 9) lie between 0.85 and 0.98, as shown in Table III.

It has also been suggested [29–31] that Equation 5 is an outcome of the hopping (of charge carriers) over the barrier (HOB). This HOB model predicts that the value of s should be given by

$$s = 1 - 6k_BT/\lambda \qquad (6)$$

where λ is the polaron binding energy. The values of s at 80 K calculated from Equation 6 using λ as twice the high-temperature activation energy, W, are shown in Table III. Good agreement between the calculated and the experimental values of s (at 80 K) is obtained. Although it is expected that s should show little temperature dependence, we could not, however, notice this thermal dependence of s from our experimental data. The values of s are also found (from Table III) to vary with V^{4+} and/or V^{5+} ion concentrations. It might be pointed out here that the simple HOB model is not sufficient for explaining both the frequency and temperature dependences of these

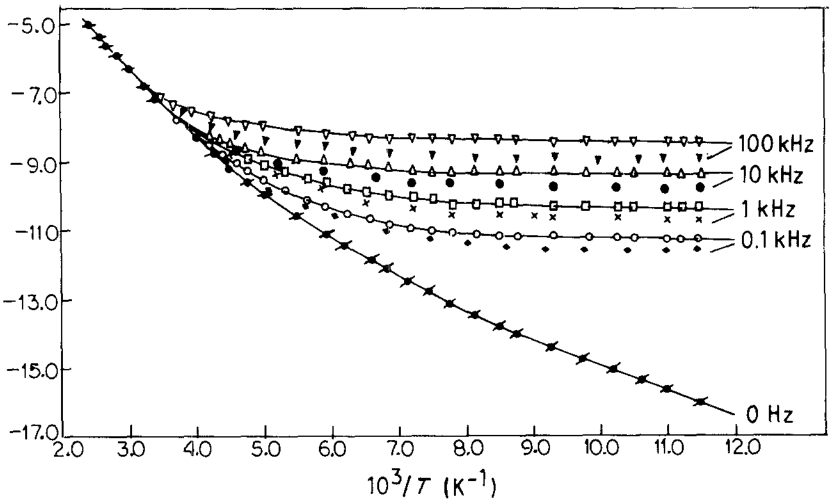

Figure 7 Thermal variation of a.c. conductivity of the VPA ⧫ and the VPG glasses with 25 mol % Sb_2O_3 (▽, △, □, ○) and GeO_2 (▲, ●, ×, ◆), respectively, at different fixed frequencies.

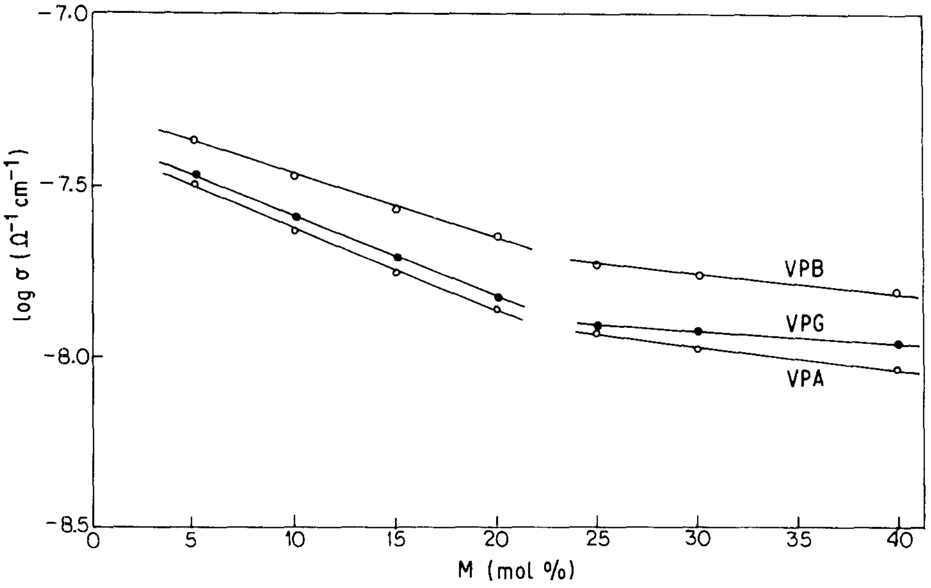

Figure 8 Variation of a.c. conductivity with concentration, x, of M (M = Bi_2O_3, Sb_2O_3, and GeO_2) of the VPB, VPA and VPG glasses, respectively, at 300 K and 10 kHz.

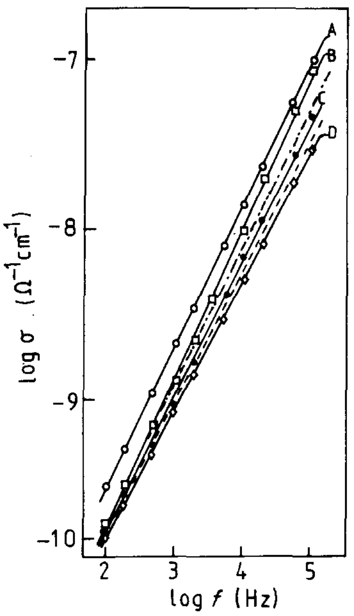

Figure 9 Frequency ($f = \omega/2\Pi$) variation of a.c. conductivity of the VPB, VPA and VPG glasses at 80 K for different concentrations of Bi_2O_3, Sb_2O_3, and GeO_2 respectively, (a) 25 mol %, (b) 40 mol % Bi_2O_3; (c) 25 mol %, (d) 40 mol % Sb_2O_3; (— . —) 25 mol %, and (- - -) 40 mol % GeO_2.

TABLE III Frequency exponent, *s*, and *N* of different glasses

Glass number	*s* at 80 K		$N (10^{22} eV^{-1} cm^{-3})$
	Experimental	Theoretical	
(VPB1)	0.93	0.89	1.00
(VPB2)	0.85	0.90	1.10
(VPB3)	0.87	0.88	1.20
(VPA1)	0.83	0.89	1.21
(VPA2)	0.94	0.89	1.17
(VPA3)	0.89	0.89	1.12
(VPG1)	0.85	0.90	1.20
(VPG2)	0.87	0.88	1.18
(VPG3)	0.84	0.89	1.13

glasses. More detailed analysis of the a.c. conductivity data of these glasses to show the frequency and temperature dependence of the exponent *s* using different theoretical models such as quantum mechanical tunnelling (QMT) [32], correlated barrier hopping (CBH) [29–31], overlapping polaron tunnelling (OPT) [32], etc., will be discussed elsewhere.

4. Conclusion

Various experimental results characterizing the properties of VPA, VPB, and VPG glasses are reported. It was found that though the general thermal behaviour of the electrical and other properties of these transition metal oxide glasses are very similar, the concentration dependences of these properties at a fixed temperature behave in different ways. Because the anomalous behaviour of $\sigma_{d,c}$ is also reflected in the a.c. conductivity, dielectric constant (ε') [5, 6], glass transition temperature (T_g), density, thermopower [5, 6], magnetic susceptibility [19], etc., at approximately the same concentration, this concentration region might be considered "critical concentration region" of many oxide glasses showing anomalous physical properties. Further studies with different glass systems have yet to be done to confirm this conjecture.

However, the reasons for these anomalies appearing in the vanadium-containing oxide glasses and also in the non-vanadate oxide glasses might be different. In the vanadate glasses the ratio V^{5+}/V^{4+} varies non-linearly with the addition of M, causing anomalous variations of the electrical and other properties. Of course, the glass-forming oxides M should have a large effect on modulating the electrical and other properties and, as a consequence, one may find noticeable differences in the properties of the VPA, and VPG glasses from those of the VPB glasses. In the non-vanadate binary PB glasses, on the other hand, the non-linear behaviour of the physical properties is attributable to the anomalous behaviour of the glass-forming oxide – the Bi_2O_3 and Sb_2O_3 in the Bi_2O_3–P_2O_5 and Sb_2O_3–P_2O_5 glasses, respectively.

In the PB glasses, for instance, the P_2O_5 is built up of an infinite network of PO_4 tetrahedra, each tetrahedron being connected at three corners to the other tetrahedra, the remaining unshared oxygen being linked to the phosphorus by a double bond. With the addition of Bi_2O_3 this vitreous structure will transform some of the P=O bonds into cross-linking bonds of the type P–O–P and Bi–O–P. This will increase the average cross-linking density of the PB glasses with further increase of Bi_2O_3 up to a "critical concentration" of 25 mol % Bi_2O_3 (for the PB glass), causing the electrical conductivity to decrease with the corresponding increase of activation energy, *W*, of the PB glasses. Beyond this "critical concentration" of Bi_2O_3, the bismuth ions may enter the glass network interstitially, causing the breaking of some network bonds (P–O–Bi or P–O–P) and subsequently being replaced by ionic bonds. This would have the effect of increasing the electrical conductivity of the PB glasses beyond 25 mol % Bi_2O_3 as indicated in Fig. 2.

Therefore, it appears that a similar situation might be responsible for the decrease or increase in electrical conduction in the VPB, VPA, and VPG glasses. The anomalous change of the ratio V^{5+}/V^{4+} might not be the real cause of the anomalous variation of the electrical and other properties of the VPA, VPB and VPG type glasses, as reported earlier by Rao [7, 8] and others [5, 6], it is actually due to the different characteristic features of the network-forming oxides and glass structure. Therefore, both the transition metal and the non-transition metal oxide glasses might show anomalous physical properties when studied as a function of concentration.

Finally, it may be concluded that although the frequency dependence of the a.c. conductivity is found to obey the general relation $\sigma_{a.c.} \propto \omega^s$, the concentration, frequency, and temperature dependences of the frequency exponent *s* behave in a more complicated manner in the VPA, VPB, and VPG glasses. However, the theoretically calculated values of *s* based on the hopping over the barrier (HOB) model, agree fairly well with the experimental values at low temperature.

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