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Electrical conductivity and ESR of lithium borate glasses containing mixed transition metal oxides

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Electron spin resonance, optical spectra and d.c. electrical conductivity of $2Li_2O \cdot 3B_2O_3$ glasses doped with V_2O_5 and CuO were investigated. Spin Hamiltonian parameters of transition metal (TM) ions have been determined. The theoretical optical basicity Λ_{th} of these glasses has been calculated and related to the spin-Hamiltonian parameters of TM ions. The variation of electrical conductivity with composition has been explained.

1. Introduction

During the last few years many papers have been published [1–5] on the electrical conductivity of oxide glasses containing single or two different transition metal (TM) oxides, which exist in the glass in two (or more) different valence states. However, only a few electrical conductivity and electron spin resonance (ESR) studies [6–10] have been reported on the same oxide glasses containing two different TM oxides.

Sayer and Lynch [3] and Chomka *et al.* [5] reported an initial decrease and then an increase in conductivity, whereas Bogomolova and Glassova [8] and Singh [9] reported an initial increase and then a decrease in conductivity, when one TM oxide is replaced by another TM oxide in a glass. It is suggested [5, 9, 10] that the increase of conductivity may be due to the hopping of electrons between TM ions of the different elements in addition to the hopping of electrons between TM ions of the same element, whereas the decrease in electrical conductivity may be due to a decrease in the redox ratio as well as to the formation of associates composed of one ion from each TM ion with one oxygen ligand.

Singh and Rokade [11] reported that conventionally quenched Li_2O–B_2O_3 (40 : 60 mol %) is the best homogeneous glass-forming composition of Li_2O and B_2O_3 with maximum conduction. In the present work we report the ESR and electrical conductivity of the fast ion conducting $2Li_2O \cdot 3B_2O_3$ glasses containing oxides of vanadium and copper, singly and in mixed proportions.

2. Experimental procedure

In the present work, Analar grade reagents of Li_2CO_3, H_3BO_3, V_2O_5 and CuO were used as starting materials for the synthesis of the glasses. The base glass composition is $2Li_2O \cdot 3B_2O_3$ to which V_2O_5 and CuO were added as given in Table I. Each batch was first sintered at 600 ± 50° C for about 5 h and then melted in a porcelain crucible in an electric muffle furnace at about 1000° C for 30 min under an air atmosphere. The melt was poured on to one carbon plate and pressed with another. First-derivative ESR spectra were recorded at room temperature (RT) (310 K) in the X-band ($\nu \sim 9.13$ GHz) on an ESR spectrometer (Varian E-112). The magnetic field was modulated at 100 kHz. DPPH with $g = 2.0036$ was used as a standard for the determination of the spin Hamiltonian parameters. ESR spectra of these samples were also recorded at liquid nitrogen temperature (LNT).

Optical transmission spectra were recorded at 310 K using a Hitachi spectrophotometer Model 330.

TABLE I Spin Hamiltonian parameters of VO^{2+} in $2Li_2O \cdot 3B_2O_3$ glasses

Glass No.	V_2O_5 (mol %)	CuO (mol %)	$g_\parallel$	$g_\perp$	$A_\parallel$ (10^{-4} cm^{-1})	$A_\perp$ (10^{-4} cm^{-1})
L1	9	–	1.9329	1.9583	166.8	53.9
L2	6	3	1.9399	1.9631	167.5	56.8
L3	4.5	4.5	1.9399	1.9685	170.3	59.7
L4	3	6	1.9399	–	173.8	–
L5	–	9	–	–		
L6	–	–	–	–		

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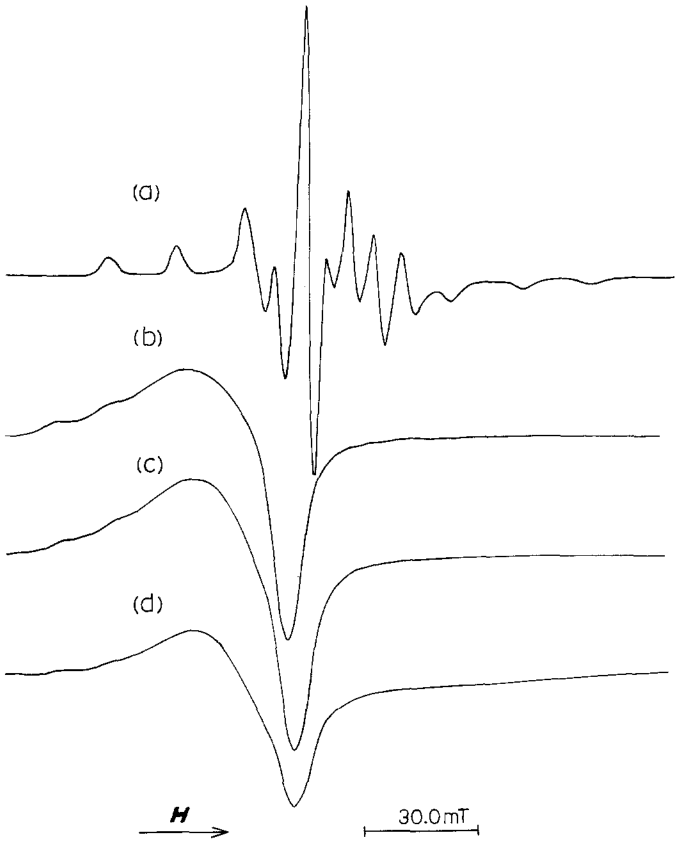

Figure 1 The ESR spectra of VO^{2+} and Cu^{2+} in the X-band ($\nu \sim 9.13$ GHz) at 310 K: (a) Glass L1, (b) Glass L2, (c) Glass L3, (d) Glass L4.

To measure the electrical conductivity, glasses in the form of slices of nearly 1 mm uniform thickness were chosen. Colloidal silver paint was used as an electrode material. A million-megohmeter Model RM 160 Mk III (BPL, India) was used to measure the d.c. conductivity. Measurements were made at different temperatures between 323 and 473 K, first by increasing and then by decreasing it. The change in the value of conductivity during the increase and the decrease of temperature was less than 5%. At any temperature it was possible to reproduce within 20% the bulk value of the conductivity when using different samples cut from the same melt of glass, or samples taken from different melts prepared under the same conditions.

The time-dependence of resistance at an applied voltage of 10 V was studied for a period up to 5 h for specimens of different composition and held at 423 K. Care was taken to see that the samples were not exposed to moisture before making the above measurements.

3. Results and discussion

ESR spectra of VO^{2+} and Cu^{2+} in Glasses L1, L2, L3 and L4 at RT (310 K) are shown in Fig. 1. The spectra at LNT did not show much difference except that the lines were sharper and more intense, which is ascribed to a spin-lattice relaxation effect. The ESR spectrum obtained for Glass L5 exhibits a pronounced peak at $g = 2.0419$ and a broad and shallow quadruplet at $g = 2.3080$, the latter arising from the splitting of $g_{\parallel}$. Such spectral features are characteristic of the Cu^{2+} ions present in the axially distorted octahedral sites.

It is seen from Fig. 1 that the hyperfine structure components due to V^{4+} in Glass L1 are well resolved, whereas only high-field hyperfine structure components due to V^{4+} and low-field hyperfine structure components due to Cu^{2+} are clearly observable in Glasses L2 and L3. In Glass L4 the resonance lines are poorly resolved. A central symmetric line was also observed in all these glasses, presumably due to Cu^{2+} ions. From the observed spectra it can be suggested that there is a considerable interaction taking place between Cu^{2+} and V^{4+} ions, simply because the hyperfine spectra of both these ions occur in the same region of the magnetic field. ESR spectra can be described by an axial spin Hamiltonian characterized by the components $g_{\parallel}$ and $g_{\perp}$ of the $\mathbf{g}$ tensor and components $A_{\parallel}$ and $A_{\perp}$ of the hyperfine tensor [12, 13]. The solutions of the spin Hamiltonian for the parallel and perpendicular components are [13]

$$\begin{aligned} B_{\parallel}(m) &= -mA_{\parallel}(1 + P') + B_{\parallel}(0)- \\ &\quad \times \{1 - 4P'[I(I + 1) - m^2(1 + P')]\}^{1/2} \end{aligned} \tag{1}$$

$$\begin{aligned} B_{\perp}(m) &= -mA_{\perp}(1 + P_1) + B_{\perp}(0) \\ &\quad \times \{1 - 4P_1[I(I + 1) - m^2(1 + P_1)]\}^{1/2} \\ &\quad - \frac{(A_{\parallel} - A_{\perp})^2}{8B_{\perp}(0)}[I(I + 1) - m^2] \end{aligned} \tag{2}$$

with

$$P' = \frac{A_{\perp}^2}{4B_{\parallel}^2(0) - A_{\parallel}^2}$$

$$P_1 = \frac{(A_{\parallel} + A_{\perp})^2}{4[4B_{\perp}^2(0) - A_{\perp}^2]}$$

where m is the magnetic quantum number of the nucleus; $B_{\parallel}(0) = h\nu/g_{\parallel}\beta$, $B_{\perp}(0) = h\nu/g_{\perp}\beta$, h is Planck's constant and β is the Bohr magneton. Here

TABLE II P, K, $A'_{\parallel}$, $A'_{\perp}$ and $\Delta g_{\parallel}/\Delta g_{\perp}$ for VO^{2+}

Glass No.	P (10^{-4}cm^{-1})	K	PK (10^{-4}cm^{-1})	$A'_{\parallel}$ (10^{-4}cm^{-1})	$A'_{\perp}$ (10^{-4}cm^{-1})	$\Delta g_{\parallel}/\Delta g_{\perp}$
L1	124.0	0.6860	85.05	81.80	31.11	1.5773
L2	122.3	0.7179	87.97	79.53	31.20	1.5918
L3	121.8	0.7496	91.30	79.00	31.60	1.8461
L4	–	–	–	–	–	–

quadrupole and nuclear Zeeman interaction terms are ignored [14, 15].

Spin Hamiltonian parameters of the V^{4+} ion determined from the observed positions of spectral lines and using Equations 1 and 2 are given in Table I. The uncertainty in the values of g is ± 0.0015 and in the values of A is 1×10^{-4}cm^{-1}. Calculated values [16] of the dipolar hyperfine coupling parameter P and the Fermi contact interaction term K are given in Table II. Further hyperfine tensor components, $A_{\parallel}$ and $A_{\perp}$, consist [17] of the contributions $A'_{\parallel}$ and $A'_{\perp}$ of the $3d_{xy}$ electrons to the hyperfine structure and the PK term arising from the anomalous contribution of the s electrons. Calculated values of $A'_{\parallel}$, $A'_{\perp}$, PK and $\Delta g_{\parallel}/\Delta g_{\perp}$ are given in Table II. It is seen from Tables I and II that $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$, $A_{\perp}$, K and $\Delta g_{\parallel}/\Delta g_{\perp}$ increase; P and $A'_{\parallel}$ decrease while $A'_{\perp}$ is approximately constant (increase is within experimental uncertainty) when V_2O_5 is replaced by CuO.

The increase in the values of K and $\Delta g_{\parallel}/\Delta g_{\perp}$ when V_2O_5 is replaced by CuO in the glasses indicates an increase in tetragonal distortion along the V^{4+}–(vanadyl oxygen) bond in the mixed glasses. The decrease in the value of $A'_{\parallel}$ for V^{4+} implies a decrease in the interaction between electron and nuclear spin moments on replacing V_2O_5 by CuO. Therefore, the progressive disappearance of the hyperfine structure could be interpreted as due to a process of nuclear relaxation in the vanadium nucleus. The decrease in $A'_{\parallel}$ may be considered as due to increasing screening of the $3d_{xy}$ orbital from its nucleus through overlap of the electron orbits of the surrounding oxygen ligands. This produces an expansion of the $3d_{xy}$ orbital resulting in a decreased interaction of this magnetic electron with the vanadium nucleus. The decrease in the value of P ($= 2\gamma\beta\beta_N\langle r^{-3}\rangle$) also suggests that the $3d_{xy}$ orbital of the magnetic electron expands when V_2O_5 is replaced by CuO.

The Cu^{2+} spectrum can be described by the same axial spin Hamiltonian as the V^{4+} ion. Spin-Hamiltonian parameters of Cu^{2+} determined by using Equations 1 and 2 are therefore given in Table III. The uncertainty in the values of g is ± 0.003 and in the values of A is $\pm 2.0 \times 10^{-4}$cm^{-1}. Since the perpendicular components were not resovled, the values of $A_{\perp}$ could not be determined. These values show that the Cu^{2+} ion is in a distorted octahedral site and the coordination structure of isolated Cu^{2+} complexes keep the same symmetry. Table III shows that $g_{\perp}$ and $A_{\parallel}$ decrease and $g_{\parallel}$ increases when CuO is replaced by V_2O_5. It can be suggested that in glasses containing mixed TM ions there is decrease of hyperfine interaction at the Cu^{2+} nucleus. A similar behaviour of the spin-Hamiltonian parameters of Cu^{2+} ions was observed in $SrO \cdot B_2O_3$ glasses [18] when CuO was replaced by V_2O_5.

The optical spectra of glasses at 310 K are shown in Fig. 2. In the spectrum of VO^{2+} for Glass L1 a broad band from 800 to 1000 nm is observed. The position of the band due to $b_2 \rightarrow e^*_{\pi}$ and $b_2 \rightarrow b^*_1$ could not be identified. In the optical spectrum of Glass L5 a single absorption band at around 800 nm is observed which can be assigned to the transition $d_{x^2-y^2} \rightarrow d_{xy}$ of the Cu^{2+} ion in a distorted octahedral site. The weak band due to the transition $d_{x^2-y^2} \rightarrow d_{yz}$, d_{zx} could not be observed. In each of the Glasses L2, L3 and L4 a band at around 770 nm is observed. Bandyopadhyay [17] also observed a band at around 770 nm in $Cu_2O \cdot V_2O_5 \cdot BaO \cdot B_2O_3$ glasses. Calculated values [19–21] of the Cu^{2+} bonding coefficients α^2 and β_1^2 are given in Table III. $A_{\parallel}$ was taken to be negative to get reasonable solutions. The bonding coefficients α^2, β_1^2 and β^2 ($= 1.00$) characterize, respectively, the in-plane σ bonding, in-plane π bonding and out-of-plane π bonding of the Cu(II) complexes: their values lie between 0.5 and 1, the limits of pure covalent and pure ionic bonding. The normalized covalencies of Cu(II)–O in-plane bonding of σ and π symmetry, Γ_{σ} and Γ_{π} are given as [22]

$$\Gamma_{\sigma} = \frac{200(1 - S)(1 - \alpha^2)}{1 - 2S}\%$$

$$\Gamma_{\pi} = 200(1 - \beta_1^2)\%$$

where S is an overlap integral between related atomic orbitals. Its value is 0.076 for oxide glasses. Calculated values of Γ_{σ} and Γ_{π} are given in Table III. It is

TABLE III Spin Hamiltonian parameters α^2, β_1^2, β^2, Γ_{σ} and Γ_{π} for Cu^{2+}

Glass No.	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ (10^{-4}cm^{-1})	α^2	β_1^2	β^2	Γ_{σ}	Γ_{π}
L2	2.3209	2.0367	157.1	0.8378	0.8064	1.00	35.35	38.72
L3	2.3188	2.0367	162.4	0.8385	0.8008	1.00	35.19	39.84
L4	2.3188	2.0386	162.4	0.8400	0.7990	1.00	34.87	40.20
L5	2.3080	2.0419	163.8	0.8308	0.7827	1.00	36.87	43.46

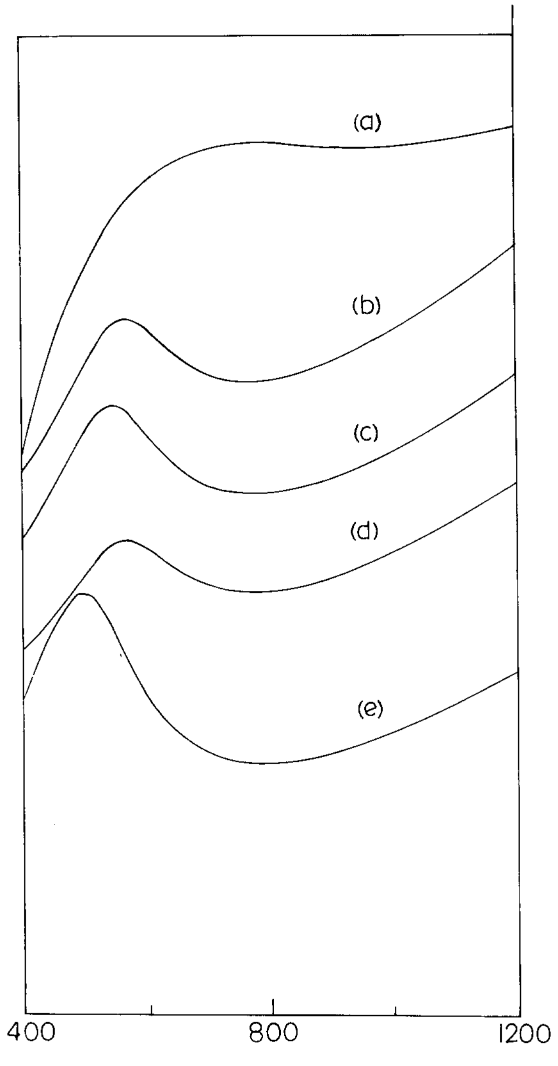

Figure 2 Optical transmission spectra of VO^{2+} and Cu^{2+} at 310 K (a) Glass L1, (b) Glass L2, (c) Glass L3, (d) Glass L4, (e) Glass L5.

clear that by replacing CuO by V_2O_5 in Glass L5 the normalized covalencies of Cu^{2+}–O and the in-plane bonding of σ symmetry (Γ_σ) and π symmetry (Γ_π) decrease.

It is also possible to calculate the theoretical optical basicity [23] given by

$$\Lambda_{th} = \sum \frac{Z_i r_i}{2\gamma_i}$$

where Z_i is the oxidation number of the cation i, r_i is the ratio of cation i with respect to the total number of oxides and γ_i is the basicity moderating parameter. γ_i for the cation is given by

$$\gamma_i = 1.36(x_i - 0.26)$$

where x_i is the Pauling electronegativity [24] of the cation. The theoretical optical basicity thus calculated is given in Table IV. The theoretical optical basicity serves in the first approximation as a measure [20] of the ability of oxygen to donate a negative charge in the glasses. In other words, the optical basicity reflects the Lewis basicity of oxide glasses. As the electron donability (i.e. Lewis basicity) of the equatorial ligands increases, σ bondings between V^{4+} and the ligands are enhanced [25]. This in turn reduces the positive charge on V^{4+} and weakens the π bondings between V^{4+} and vanadyl oxygen. This increases the bond length V^{4+}–(vanadyl oxygen). Consequently the octahedral symmetry is improved. In the present work we find that the tetragonal distortion along the V^{4+}–(vanadyl oxygen) bond increases with a decrease in Λ_{th}.

In general the normalized covalency of Cu(II)–O in-plane bonding of π symmetry Γ_π increases [20] with increasing optical basicity. However, in the present study of borate glasses containing mixed transition metal oxides, we find that Γ_π increases with decrease in the theoretical optical basicity.

Fig. 3 shows the variation of $\log\sigma$ (σ is the electrical conductivity) against $10^3/T$ for lithium borate glasses containing single and mixed TM ions. In general the variation of the conductivity of the samples over an accessible temperature range of about 200 K is more than three orders of magnitude in all these glasses. From Fig. 3 the following observations can be made:

(i) The electrical conductivity increases with increase in temperature.

(ii) At all temperatures the conductivity of undoped lithium borate glass L6, is maximum.

(iii) At all temperatures the conductivity of Glass L1 is more than that of L5.

(iv) Below 373 K the conductivity of the glass decreases when V_2O_5 is replaced by CuO from L1 to L4, i.e. $\sigma_{L1} > \sigma_{L2} > \sigma_{L3} > \sigma_{L4}$. Typical conductivity values at 348 K are given in Table IV.

(v) Above 373 K the conductivities of Glasses L3, L2, L1, L4 and L5 are in decreasing order. Typical conductivity values at 448 K are given in Table IV.

We may consider that $\log\sigma$ against $10^3/T$ plots are linear, satisfying the equation

$$\sigma = \sigma_0 \exp(-W/kT)$$

where σ is the conductivity, σ_0 is a constant for a given glass and k is Boltzmann's constant; T is the absolute temperature and W is the activation energy for conduction. Table IV lists the derived values of the activation

TABLE IV Theoretical optical basicity Λ_{th}, and σ and activation energy W

Glass No.	Λ_{th}	W (eV)	σ ($\Omega^{-1}cm^{-1}$)	
			348 K	448 K
L1	0.5321	0.60	6.71×10^{-9}	2.30×10^{-7}
L2	0.5300	0.56	3.70×10^{-9}	2.47×10^{-7}
L3	0.5289	0.61	3.04×10^{-9}	3.34×10^{-7}
L4	0.5278	0.73	8.13×10^{-10}	2.11×10^{-7}
L5	0.5254	0.73	1.14×10^{-9}	1.99×10^{-7}
L6	–	0.53	1.12×10^{-8}	8.62×10^{-7}

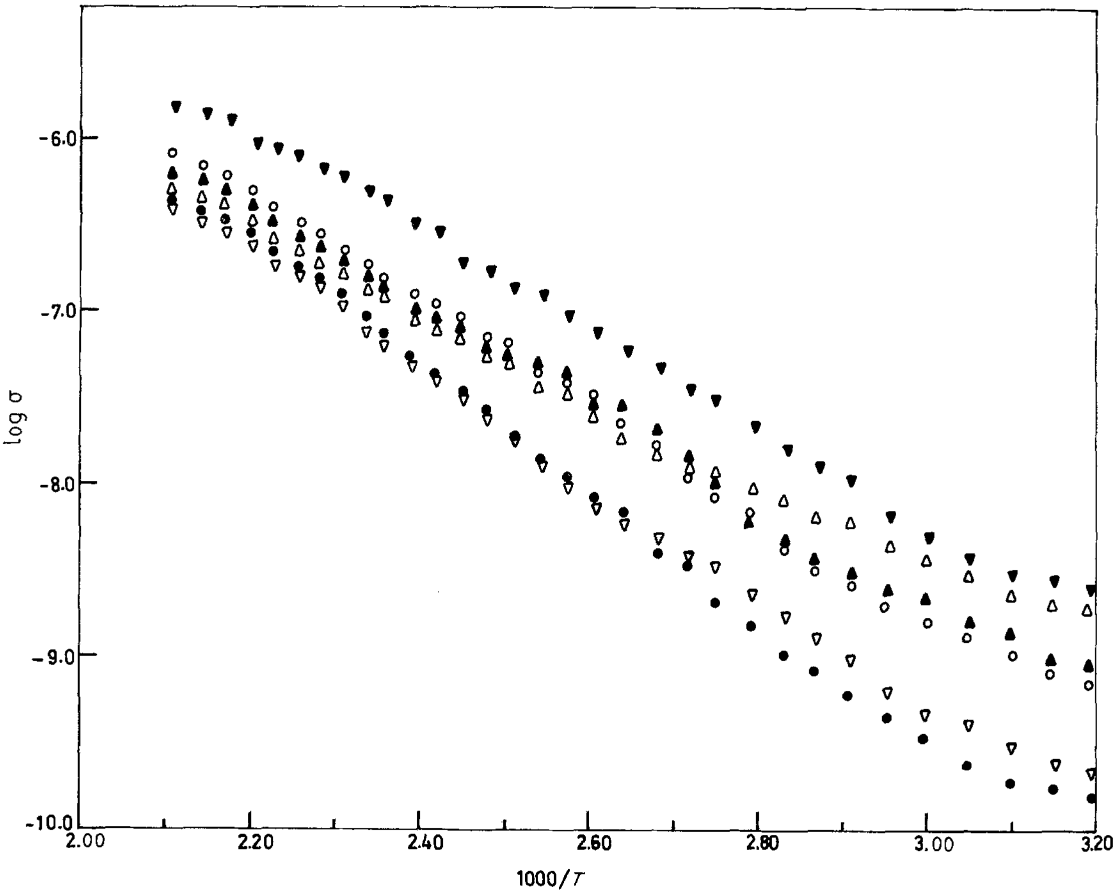

Figure 3 Variation of log σ as a function of $1000/T$ for (△) Glass L1, (▲) Glass L2, (○) Glass L3, (●) Glass L4, (▽) Glass L5, (▼) Glass L6.

energy for different composition. It is found that the activation energy of Glass L6 is the lowest.

The time-dependence of resistance at an applied voltage of 10 V was studied for a period up to 5 h for these glasses at 423 K and is shown in Fig. 4. As a general rule the resistance of all six glasses increased over these extended periods, suggesting that the conductivity was predominantly ionic. Since the TM ions exist in more than one valence state (e.g. V^{4+}, V^{5+} and Cu^{1+}, Cu^{2+}), so conduction could also take place by the transfer of electrons from low to high valence states. Therefore the measured electrical conductivity may have a small contribution from electronic conductivity.

The conductivity of Glass L6 is pure ionic. The addition of 9 mol % CuO in $2Li_2O \cdot 3B_2O_3$ reduces the molar percentage of Li_2O in Glass L5. A decrease of Li_2O decreases the electrical conductivity and increases activation energy rapidly. There may be a small contribution to the conductivity by the transfer of electrons

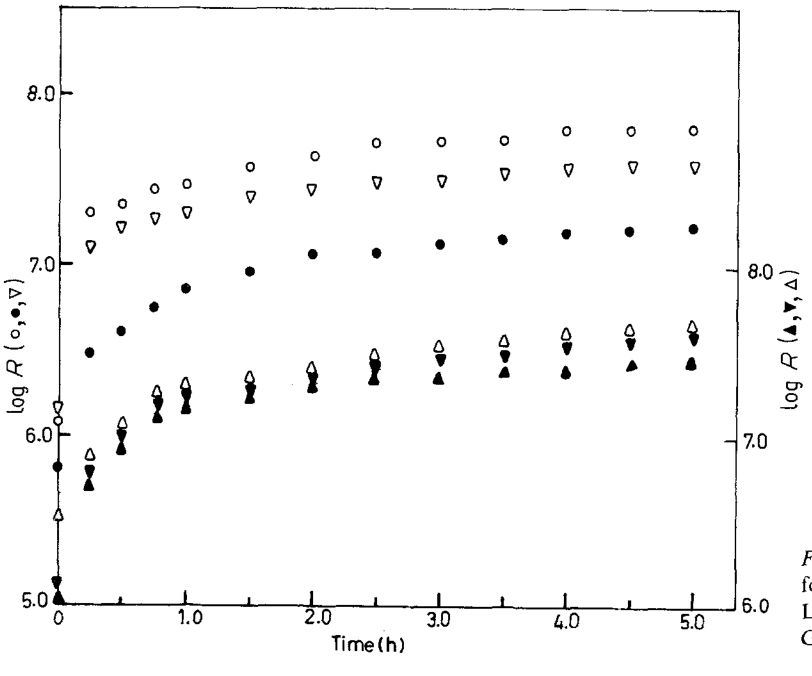

Figure 4 Resistance at 423 K as a function of time for constant voltage 10 V: (○) Glass L1, (●) Glass L2, (▽) Glass L3, (▲) Glass L4, (▼) Glass L5, (△) Glass L6.

from Cu^{1+} to Cu^{2+}. Electronic conductivity due to the hopping of electrons in Glass L5 does not play an important role. Therefore σ_{L5} is less than σ_{L6} and the activation energy of L5 is more than the activation energy of L6. The addition of 9 mol % of V_2O_5 in $2Li_2O \cdot 3B_2O_3$ for L1 glass gives rise to the formation [26] of $LiVO_3$ and the three-dimensional bonding of the glass network decreases. A decrease of Li_2O reduces the ionic conductivity. The electronic conductivity due to $V^{4+} \rightarrow V^{5+}$ does not play an important part in the total conductivity of L1. Therefore σ_{L1} is less than σ_{L6} and the activation energy of L1 is more than the activation energy of L6. Similarly the molar percentage of Li_2O in Glasses L2, L3 and L4 is less than in Glass L6, which reflects the fact that at all temperatures of the present investigation the decrease of ionic conductivity in L2, L3 and L4 is not compensated by the electronic conductivity due to hopping of electrons between ions of the same TM element and between the ions of the different TM elements. This explains why Li_2O–B_2O_3 is suitable for preparing superionic conducting glasses.

The conductivity of $2Li_2O \cdot 3B_2O_3$ glass containing V_2O_5 is more than the conductivity of $2Li_2O \cdot 3B_2O_3$ glass containing the same amount of CuO. This may be seen as V_2O_5 behaving like B_2O_3 in the preparation [27] of superionic conducting glasses, whereas copper ions are glass-modifiers and they may show a "blocking effect" on the overall mobility of lithium ions. A similar argument was considered by Khawaja *et al.* [27] for the decrease in the conductivity of sodium germanate glass when copper is added to it. This also explains the decrease in conductivity ($\sigma_{L2} > \sigma_{L3} > \sigma_{L4}$) of $2Li_2O \cdot 3B_2O_3$ glass when V_2O_5 is replaced by CuO at temperatures below 373 K. Above 373 K the conductivity of L3 is more than the conductivity of L2 and L4. The reason for this may be that at high temperature the contribution to conductivity from the hopping of electrons in $Cu^{1+} \rightarrow V^{4+}$, $V^{4+} \rightarrow Cu^{2+}$, $Cu^{1+} \rightarrow Cu^{2+}$ and $V^{4+} \rightarrow V^{5+}$ is maximum for Glass L3 in which the molar percentage of V_2O_5 is equal to that of CuO. At low temperature this contribution may not be appreciable. However, the activation energy of Glass L2 is less than that of any other $2Li_2O \cdot 3B_2O_3$ glass containing TM ions, but we find that the pre-exponential term σ_0 for L2 is very small as compared to σ_0 for L3, which gives $\sigma_{L3} > \sigma_{L2}$.

It can be concluded that the conductivity of $2Li_2O \cdot 3B_2O_3$ glass is predominantly ionic. The addition of V_2O_5 and/or CuO decreases its conductivity.

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