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Effect of Bi_2O_3 on EPR, optical transmission and DC conductivity of vanadyl doped alkali bismuth borate glasses

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Abstract

Glasses with composition $x\,Bi_2O_3 \cdot (30 - x)M_2O \cdot 70B_2O_3$ (M = Li, Na) containing 2 mol% V_2O_5 have been prepared over the range $0 \leq x \leq 15$ (x is in mol%). The electron paramagnetic resonance spectra of VO^{2+} of these glasses have been recorded in the X-band (≈ 9.3 GHz) at room temperature (RT ≈ 300 K). Spin Hamiltonian parameters, $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$, $A_{\perp}$, dipolar hyperfine coupling parameter, P, and Fermi contact interaction parameter, K, have been calculated. The molecular orbital coefficients, α^2 and γ^2, have been calculated by recording the optical transmission spectra. In $x\,Bi_2O_3 \cdot (30 - x)Li_2O \cdot 70B_2O_3$ glasses there is decrease in the tetragonality of the $V^{4+}O_6$ complex for x up to 6 mol% whereas for $x \geq 6$ mol%, tetragonality increases. In $x\,Bi_2O_3 \cdot (30 - x)Na_2O \cdot 70B_2O_3$ glasses there is increase in the tetragonality of the $V^{4+}O_6$ complex with increasing x. The $3d_{xy}$ orbit expands with increase in $Bi_2O_3{:}M_2O$ ratio. Values of the theoretical optical basicity, Λ_{th}, have also been reported. The DC conductivity increases with increase in temperature. The order of conductivity is 10^{-5} ohm^{-1} m^{-1} at low temperature and 10^{-3} ohm^{-1} m^{-1} at high temperature. The DC conductivity decreases and the activation energy increases with increase in $Bi_2O_3{:}M_2O$ ratio.
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1. Introduction

Electron paramagnetic resonance (EPR) spectroscopy is a sensitive technique for the study of transition metal (TM) ions in solids. It provides information concerning the valence state of TM ions, their concentration, local environment and the nature of interactions between them. In recent years glasses doped with TM ions have attracted a great deal of attraction because of their potential applications in the development of new tunable solid-state lasers, solar energy convectors, and fiber optic communication devices. Several authors have conducted studies on EPR spectra of single TM ions in oxide glasses [1–7]. Further, the glasses with high ionic conductivity presently attract considerable scientific interest because of their potential applications as solid electrolytes in various electrochemical devices such as solid-state batteries, fuel cells, memory devices and chemical sensors [8–10]. Alkali or alkaline earth cations incorporated in the structure of glasses are responsible for ionic conduction in these materials [11,12]. The highest conductivities are observed with monovalent cations such as alkali or silver ions. In earlier studies [1,4], it was observed that in ternary borate glasses ($CoO \cdot Na_2O \cdot B_2O_3$ and $NiO \cdot Li_2O \cdot B_2O_3$) containing 2.0 mol% of V_2O_5 electrical conductivity decreases with increase in $CoO{:}Na_2O$ ($NiO{:}Li_2O$) ratio, and Co and Ni showed a blocking effect on the overall mobility of alkali ions. The purpose

Table 1
Spin Hamiltonian parameters of VO^{2+} at room temperature and Λ_{th} in $x\,Bi_2O_3\cdot(30-x)Li_2O\cdot70B_2O_3$ glasses

Glass no.	x (mol%)	V_2O_5 (mol%)	$g_\parallel$ (± 0.001)	$g_\perp$ (± 0.001)	$\lvert A_\parallel\rvert$ (10^{-4} cm^{-1}) (± 1.0)	$\lvert A_\perp\rvert$ (10^{-4} cm^{-1}) (± 1.0)	Λ_{th}
1L	0	2	1.9391	1.9736	169.02	59.89	0.4607
2L	2	2	1.9377	1.9721	168.71	59.84	0.4580
3L	4	2	1.9378	1.9721	168.72	59.85	0.4555
4L	6	2	1.9391	1.9707	168.38	59.80	0.4531
5L	8	2	1.9406	1.9733	168.88	60.34	0.4508
6L	10	2	1.9392	1.9736	168.75	60.35	0.4485
7L	12	2	1.9392	1.9736	168.75	60.35	0.4464
8L	15	2	1.9392	1.9736	168.84	61.27	0.4433

$\lvert A_\parallel\rvert$ and $\lvert A_\perp\rvert$ are negative.

of the present paper is to study the effect of Bi_2O_3 on the features of EPR spectra of the VO^{2+} doped in $x\,Bi_2O_3\cdot(30-x)M_2O\cdot70B_2O_3$ (M = Li, Na) ($0 \leq x \leq 15$, x is in mol%) glasses and to study the effect of Bi_2O_3 on the electrical conductivity of the vanadyl doped alkali borate glasses.

2. Experimental

2.1. Glass preparation

The starting materials used were Analar grade reagents of Li_2CO_3, Na_2CO_3, H_3BO_3, Bi_2O_3 and V_2O_5. Tables 1 and 3 present the mol% composition of the glasses studied. To each batch 2 mol% of V_2O_5 was added. Reagents of appropriate proportions were melt in porcelain crucibles at about 1273 K in an electrical muffle furnace for half an hour. The melt was stirred occasionally for proper mixing. After the disappearance of all the bubbles, the melt was quickly poured onto a carbon plate and pressed with another.

2.2. EPR measurements

The first derivative EPR spectra of the crushed samples were recorded at room temperature (RT) in the X-band (≈ 9.3 GHz) on an EPR spectrometer (Varian E-109) using 10.0 mW microwave power. A magnetic field modulation of 100 kHz with a peak to peak (p–p) amplitude of 0.1 mT was applied. Polycrystalline DPPH was used as a standard g marker ($g = 2.0036 \pm 0.0002$).

2.3. Optical transmission measurements

Th optical transmission spectra of the as-prepared samples were recorded at RT using Perkin-Elmer UV/VIS spectrometer (Lambda 20) in the wavelength range 500–850 nm.

2.4. DC conductivity measurement

For the electrical conductivity measurements, silver paste electrodes were used on uniformly thick glass (thickness approximately 1.0 mm) slices. The measurements were made by the standard technique in the temperature range 300–523 K first by increasing the temperature and then decreasing it. Measurements of DC conductivity were carried out using the device described by Khasa et al. [1]. A constant voltage of 10 V is applied across the sample and circulating current was measured by using a Kiethley 617 programmable electrometer/source.

3. Results

3.1. EPR

Fig. 1 shows the EPR spectra of the VO^{2+} in $Bi_2O_3\cdot Li_2O\cdot B_2O_3$ glass samples 1L, 3L, 5L, and 7L. Similar spectra were obtained for other samples. These spectra of the glasses show features very similar to those found in various alkali borate glasses containing vanadium [2–4]. The spectra have structures which are characteristic of a hyperfine interaction arising from an unpaired electron with the ^{51}V nucleus whose spin is 7/2. These spectra were analysed by assuming [5–7] that vanadium is present as vanadyl ion in a ligand field of C_{4V} symmetry. The spin Hamiltonian used is of the form [2]

$$\mathscr{H} = \beta g_\parallel B_z S_z + \beta g_\perp (B_x S_x + B_y S_y) + A_\parallel S_z I_z \\ + A_\perp (S_x I_x + S_y I_y), \qquad (1)$$

where the symbols have their usual meaning and quadrupole and nuclear Zeeman interaction terms are ignored. The solutions [3] of the spin Hamiltonian (1) are given in Eqs. (2) and (3) for the parallel and perpendicular orientations, respectively,

$$B_\parallel(m) = B_\parallel(0) - mA_\parallel - \{(63/4) - m^2\}A_\perp^2/2B_\parallel(0), \qquad (2)$$

$$B_\perp(m) = B_\perp(0) - mA_\perp - \{(63/4) - m^2\}$$
$$\times (A_\parallel^2 + A_\perp^2)/4B_\perp(0), \tag{3}$$

where m is the magnetic quantum number of the vanadium nucleus having values $\pm 7/2$, $\pm 5/2$, $\pm 3/2$ and $\pm 1/2$ and

$$B_\parallel(0) = h\nu/g_\parallel\beta \text{ and } B_\perp(0) = h\nu/g_\perp\beta,$$

where h is the Planck constant, ν is the frequency of the spectrometer and β is the Bohr magneton. Measurements for the $B_\parallel$ position were taken which correspond to a maximum in the first derivative curve of the parallel hyperfine structure (hfs) component for a given m value, whereas the $B_\perp$ position is enclosed between the first derivative perpendicular peak and its 'zero' [2]. Spin Hamiltonian parameters of the VO^{2+} ion were determined from the observed

positions of the lines and by using Eqs. (2) and (3) for all samples and are reported in Tables 1 and 3. The uncertainty in the value of g is ± 0.001 and in the value of A is $\pm 1.0 \times 10^{-4}$ cm^{-1} to satisfy the calculated value of line position with the corresponding experimental value. From the values of these parameters, the dipolar hyperfine coupling parameter, $P = 2\gamma\beta_e\beta_N\langle r^{-3}\rangle$ and the Fermi contact interaction term, K, are evaluated using the expressions developed by Kivelson and Lee [13]

$$A_\parallel = -P[K + 4/7 - \Delta g_\parallel - (3/7)\Delta g_\perp], \tag{4}$$

$$A_\perp = -P[K - 2/7 - (11/14)\Delta g_\perp], \tag{5}$$

where $\Delta g_\parallel = g_\parallel - g_e$; $\Delta g_\perp = g_\perp - g_e$ and $g_e(= 2.0023)$ is the g factor of free electrons [14,15]. Both $A_\parallel$ and $A_\perp$ are found to be negative by the method proposed by Muncaster
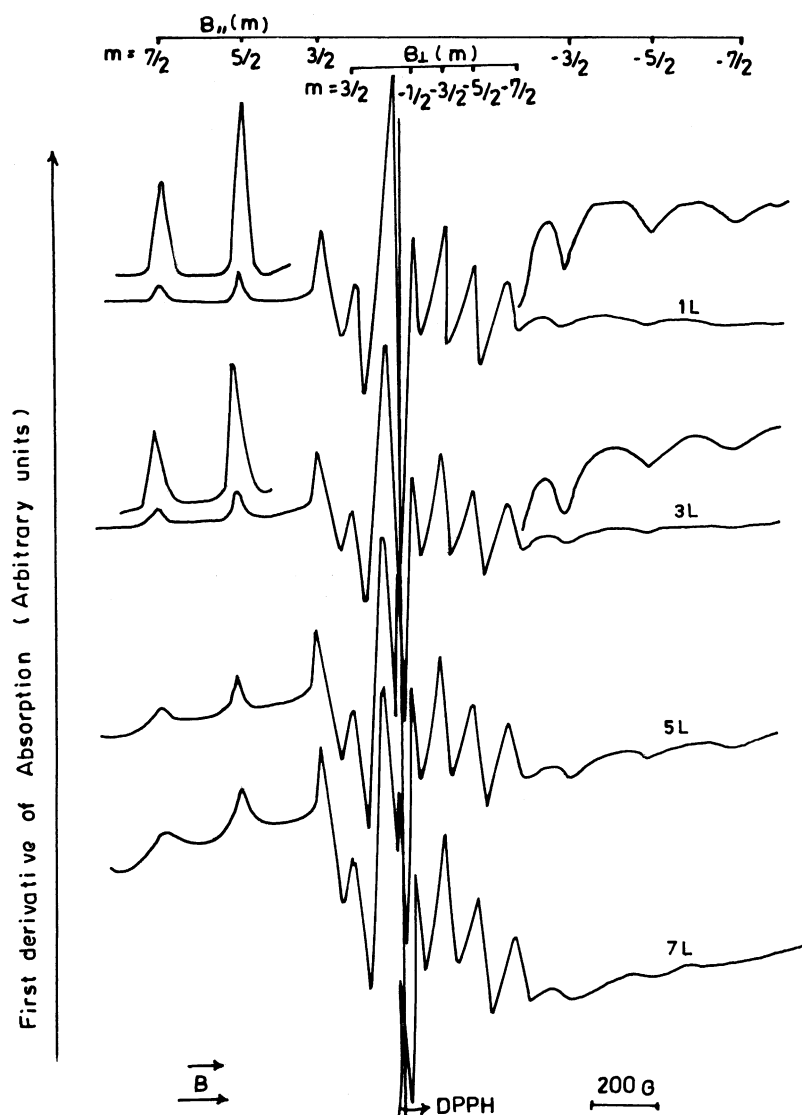

Fig. 1. The EPR spectra of VO^{2+} ions in Bi$_2$O$_3$·Li$_2$O·B$_2$O$_3$ glasses in the X-band ($\nu \sim 9.3$ GHz) at RT.

Table 2
P, K, $|A'_\parallel|$, $|A'_\perp|$, $\Delta g_\parallel/\Delta g_\perp$, α^2 and γ^2 of VO^{2+} in $x\,Bi_2O_3\cdot(30-x)Li_2O\cdot70B_2O_3$ glasses at room temperature

Glass no.	P (10^{-4} cm^{-1})	K	$|A'_\parallel|$ (10^{-4} cm^{-1})	$|A'_\perp|$ (10^{-4} cm^{-1})	$\Delta g_\parallel/\Delta g_\perp$	α^2	γ^2
1L	119.92	0.7625	77.58	31.55	2.1982	0.5659	0.7466
2L	119.51	0.7627	77.56	31.31	2.1395	0.5784	0.7856
3L	119.53	0.7627	77.56	31.32	2.1396	0.5775	0.7856
4L	119.45	0.7615	77.42	31.16	1.9987	0.5659	0.8221
5L	119.48	0.7680	77.12	31.42	2.1288	0.5525	0.7544
6L	119.13	0.7697	77.05	31.35	2.1983	0.5650	0.7466
7L	119.13	0.7697	77.05	31.35	2.1983	0.5650	0.7466
8L	118.22	0.7814	76.46	31.11	2.1983	0.5650	0.7466

Table 3
Spin Hamiltonian parameters of VO^{2+} at room temperature and Λ_{th} in $x\,Bi_2O_3\cdot(30-x)Na_2O\cdot70B_2O_3$ glasses

Glass no.	x (mol%)	V_2O_5 (mol%)	$g_\parallel$ (± 0.001)	$g_\perp$ (± 0.001)	$|A_\parallel|$ (10^{-4} cm^{-1}) (± 1.0)	$|A_\perp|$ (10^{-4} cm^{-1}) (± 1.0)	Λ_{th}
1N	0	2	1.9408	1.9724	167.62	58.47	0.4710
2N	2	2	1.9408	1.9724	167.63	58.93	0.4675
3N	4	2	1.9393	1.9721	168.68	59.84	0.4641
4N	6	2	1.9394	1.9721	168.68	59.85	0.4608
5N	8	2	1.9400	1.9724	168.73	59.86	0.4577
6N	10	2	1.9400	1.9724	168.73	60.31	0.4547
7N	12	2	1.9409	1.9739	169.17	60.82	0.4519
8N	15	2	1.9393	1.9735	169.04	61.27	0.4478

$|A_\parallel|$ and $|A_\perp|$ are negative.

and Parke [16]. The term $-PK$ in Eqs. (4) and (5) is due to the s-character of the magnetic spin of the vanadium. Basically this s-character results from the partial unpairing or polarization of the inner s electrons as a result of an interaction with the unpaired d electrons [17]. The estimate of this polarization was made by Heine [17] and the contribution to the hyperfine coupling due to the term $-PK$ is included. For transition metal ions, K is found to be positive [15]. From the molecular orbital theory, it can also be shown [14] that the components $A_\parallel$ and $A_\perp$ consist of the contributions $A'_\parallel$ and $A'_\perp$ of the $3d_{xy}$ electron to the hyperfine structure and the PK term arises due to the anomalous contribution of the s-electrons. Eqs. (4) and (5) may be

rewritten in the following way:

$$A_\parallel = -PK - P[4/7 - \Delta g_\parallel - (3/7)\Delta g_\perp] = -PK + A'_\parallel, \quad (6)$$

$$A_\perp = -PK + P[2/7 + (11/14)\Delta g_\perp] = -PK + A'_\perp. \quad (7)$$

The values of $A'_\parallel$ and $A'_\perp$ were calculated and are given in Tables 2 and 4. The values of $\Delta g_\parallel/\Delta g_\perp$, which measures the tetragonality of the vanadium site [14], are also included in Tables 2 and 4.

Theoretical optical basicity, Λ_{th}, is also calculated [18] by using the expression

$$\Lambda_{th} = \sum_i (Z_i r_i / 2\gamma_i), \quad (8)$$

Table 4
P, K, $|A'_\parallel|$, $|A'_\perp|$, $\Delta g_\parallel/\Delta g_\perp$, α^2 and γ^2 of VO^{2+} in $x\,Bi_2O_3\cdot(30-x)Na_2O\cdot70B_2O_3$ glasses at room temperature

Glass no.	P (10^{-4} cm^{-1})	K	$|A'_\parallel|$ (10^{-4} cm^{-1})	$|A'_\perp|$, (10^{-4} cm^{-1})	$\Delta g_\parallel/\Delta g_\perp$	α^2	γ^2
1N	120.22	0.7486	77.63	31.52	2.0580	0.5517	0.7728
2N	119.72	0.7545	77.30	31.39	2.0580	0.5517	0.7728
3N	119.69	0.7620	77.48	31.35	2.0844	0.5651	0.7806
4N	119.70	0.7620	77.48	31.36	2.0844	0.5642	0.7806
5N	119.81	0.7618	77.46	31.42	2.0859	0.5588	0.7728
6N	119.30	0.7676	77.13	31.28	2.0859	0.5588	0.7728
7N	119.28	0.7733	76.94	31.41	2.1620	0.5508	0.7341
8N	118.45	0.7803	76.60	31.16	2.1885	0.5651	0.7444

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

$$\gamma_i = 1.36(x_i - 0.26), \tag{9}$$

where x_i is the Pauling electronegativity [19] of the cation. The calculated values of Λ_{th} of samples are given in Tables 1 and 3.

3.2. Optical transmission

For all the glasses only two transmission band are observed. Fig. 2 shows optical transmission spectra of sample nos 1L and 2L. For all the $Bi_2O_3 \cdot Li_2O \cdot B_2O_3$ samples under study these bands are at 560 and at 771 nm whereas for $Bi_2O_3 \cdot Na_2O \cdot B_2O_3$ samples these bands are at 559 and 776 nm. These transmission bands are typically for VO^{2+} and can be assigned to $b_2 \rightarrow b_1^*$ and $b_2 \rightarrow e_{II}^*$ transitions, respectively. The values of $g_\parallel$ and $g_\perp$ are related to bonding parameters by the following equations [14]

$$(1 - \alpha^2) = 1 - [1 - g_\parallel/g_e]E_2/4\lambda\beta^2, \tag{10}$$

$$(1 - \gamma^2) = 1 - [1 - g_\perp/g_e]E_1/\lambda\beta^2, \tag{11}$$

where E_1 and E_2 are the energy of transitions $(b_2 \rightarrow e_{II}^*)$ and $(b_2 \rightarrow b_1^*)$, respectively. β^2 is a measure of the in-plane π bonding with the equilateral ligands and is assumed to be equal to 1 for many glasses containing VO^{2+} ion [18]. λ is the spin orbit coupling constant and is equal to 249 cm^{-1} [16]. $(1 - \alpha^2)$ and $(1 - \gamma^2)$ indicate the covalency rates. Using Eqs. (10) and (11) the values of α^2 and γ^2 were calculated and are given in Tables 2 and 4.

3.3. DC conductivity

Figs. 3 and 4 show the temperature dependence of the DC conductivity of the $x Bi_2O_3 \cdot (30 - x)Li_2O \cdot 70B_2O_3$ ($0 \leq x \leq 15$) and $x Bi_2O_3 \cdot (30 - x) \cdot Na_2O \cdot 70B_2O_3$ ($0 \leq x \leq 15$) glasses, respectively. The linear relationship between the logarithm of DC conductivity (log σ, σ is expressed in
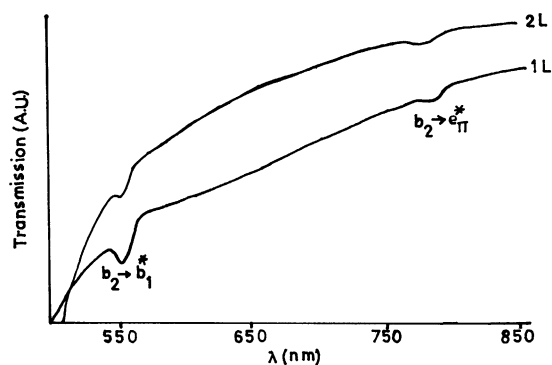

Fig. 3. Variation of log σ versus $10^3 T^{-1}$ for $x Bi_2O_3 \cdot (30 - x)Li_2O \cdot 70B_2O_3$ glasses.

ohm^{-1} m^{-1}) and inverse of temperature with a negative slope indicates that the following well-known Arrhenius law is satisfied

$$\sigma = \sigma_0 \exp(-W/kT), \tag{12}$$

where σ_0 is a constant for a given glass, 'k' is the Boltzmann constant and W is the activation energy for conduction. The values of W and pre-exponential term, σ_0, were evaluated by using the least square fitting of the experimental data with the relation

$$\log \sigma = \log \sigma_0 - (W/1000k)(1000/T). \tag{13}$$

Values of W, log σ_0 and σ at 523 and at 423 K are given in Tables 5 and 6. From these tables and Figs. 3 and 4, it is observed that the DC conductivity increases with increase in temperature and it decreases when Li_2O is replaced by Na_2O
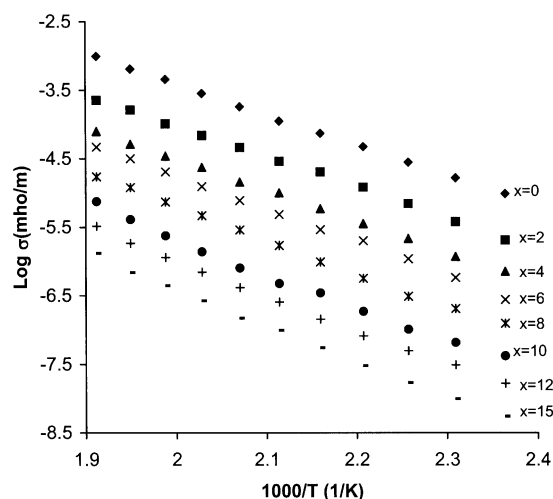

Fig. 2. The optical transmission spectra of VO^{2+} ions in glass nos 1L and 2L at RT.

Fig. 4. Variation of log σ versus $10^3 T^{-1}$ for $x Bi_2O_3 \cdot (30 - x)Na_2O \cdot 70B_2O_3$ glasses.

Table 5
DC conductivity, σ and activation energy, W of $x\,Bi_2O_3\cdot(30 - x)Li_2O\cdot70B_2O_3$ glasses

Glass no.	x (mol%)	V_2O_5 (mol%)	$\sigma_{at\ 423K}$ $(\Omega^{-1}m^{-1})$	$\sigma_{at\ 523K}$ $(\Omega^{-1}m^{-1})$	W (eV)
1L	0	2	4.83×10^{-5}	3.62×10^{-3}	0.82
2L	2	2	1.41×10^{-5}	1.43×10^{-3}	0.88
3L	4	2	4.39×10^{-6}	5.12×10^{-4}	0.92
4L	6	2	9.02×10^{-7}	1.83×10^{-4}	1.00
5L	8	2	5.18×10^{-7}	9.69×10^{-5}	1.00
6L	10	2	1.32×10^{-7}	3.45×10^{-5}	1.05
7L	12	2	5.43×10^{-8}	1.44×10^{-5}	1.08
8L	15	2	1.30×10^{-8}	3.79×10^{-6}	1.10

at constant concentration of B_2O_3 and Bi_2O_3. The increase in conductivity is of the order of 100 times when temperature is raised from 423 to 523 K. Fig. 5 indicates that the activation energy increases with increase in Bi_2O_3.

4. Discussion

4.1. EPR

In materials containing vanadyl ion, although the V^{4+} ion is usually six co-ordinated, its local symmetry is generally a distorted octahedron of oxygen ions, i.e. the bond length between the vanadium and the vanadyl oxygen is extraordinarily short compared with its bond length with other ligands. Hecht and Johnston [2] studied extensively the EPR and optical spectra of V^{4+} ion in soda boric oxide glasses and observed that the vanadyl exists in the sample with one of the two possible symmetries, i.e. threefold symmetry or fourfold symmetry. An octahedral site symmetry with tetragonal compression would give $g_{\parallel} < g_{\perp} < g_e$ and $|A_{\parallel}| > |A_{\perp}|$ [2]. The values of SHP obtained in the present study satisfy these observations. Thus it may be concluded that V^{4+} ions in these glasses exist as VO^{2+} ions

Table 6
DC conductivity, σ and activation energy, W of $x\,Bi_2O_3\cdot(30 - x)Na_2O\cdot70B_2O_3$ glasses

Glass no.	x (mol%)	V_2O_5 (mol%)	$\sigma_{at\ 423K}$ $(\Omega^{-1}m^{-1})$	$\sigma_{at\ 523K}$ $(\Omega^{-1}m^{-1})$	W (eV)
1N	0	2	9.67×10^{-6}	9.81×10^{-4}	0.88
2N	2	2	2.05×10^{-6}	2.26×10^{-4}	0.89
3N	4	2	7.16×10^{-7}	7.97×10^{-5}	0.90
4N	6	2	2.76×10^{-7}	4.67×10^{-5}	0.96
5N	8	2	1.24×10^{-7}	1.72×10^{-5}	0.97
6N	10	2	6.56×10^{-8}	7.48×10^{-6}	0.98
7N	12	2	3.11×10^{-8}	3.27×10^{-6}	1.00
8N	15	2	9.92×10^{-9}	1.32×10^{-6}	1.03
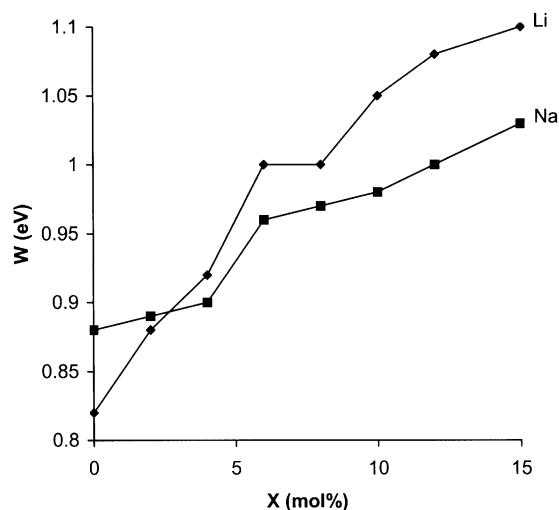
Fig. 5. Variation of activation energy, W versus mol% of Bi_2O_3 in $x\,Bi_2O_3\cdot(30 - x)M_2O\cdot70B_2O_3$ (M = Li, Na) glasses.

in octahedral coordination with a tetragonal compression and belong to C_{4V} symmetry. Tables 1 and 2 show that the change in the values of $g_{\parallel}$ and $|A_{\parallel}|$ is within experimental error when Li_2O is replaced by Bi_2O_3, whereas $g_{\perp}$, K and $\Delta g_{\parallel}/\Delta g_{\perp}$ show a minima for the glass no. 4L. The decrease in the value of $\Delta g_{\parallel}/\Delta g_{\perp}$ for x up to 6 mol% indicates that the octahedral symmetry is improved at V^{4+} ion site. For further increase in the mol% of Bi_2O_3 the value of $\Delta g_{\parallel}/\Delta g_{\perp}$ increases which indicates that the octahedral symmetry is reduced at V^{4+} ion site. As suggested by Kivelson and Lee [13], we assume that the decrease in the value of K up to $x = 6$ mol% is due to [20–22] a decrease in the tetragonal nature of the $V^{4+}O_6$ complex because of a strongly bonded oxygen at the V^{4+} ion in the site opposite to the vanadyl oxygen. The increase in K for $6 \leq x \leq 15$ mol% is due to an increase in the tetragonal nature of the $V^{4+}O_6$ complex [1]. The decrease of the anisotropic contribution (i.e. $|A'_{\parallel}|$ and $|A'_{\perp}|$) of the $3d_{xy}$ electron to the hyperfine splitting is brought about by increasing [14] screening of the $3d_{xy}$ orbital from its nucleus through overlap of the electron orbits of the surrounding oxygen ligands. This screening produces an expansion of the $3d_{xy}$ orbital, resulting in a decreased interaction between this magnetic electron with the vanadium nucleus. Decrease in the value of P also supports the argument that the $3d_{xy}$ orbit expands with increase in $Bi_2O_3:Li_2O$ ratio.

Tables 3 and 4 show that the values of $g_{\perp}$, $|A_{\parallel}|$, $|A_{\perp}|$, K and $\Delta g_{\parallel}/\Delta g_{\perp}$ increase and values of P, $|A'_{\parallel}|$ and $|A'_{\perp}|$ decrease when Na_2O is replaced by Bi_2O_3. The change in $g_{\parallel}$, is within experimental error. Increase in the value of K with increase in $Bi_2O_3:Na_2O$ ratio is due to increase [20–22] in tetragonal nature of the $V^{4+}O_6$ complex because of strongly bonded oxygen at the V^{4+} ion in the site opposite to the vanadyl oxygen. The increase in $\Delta g_{\parallel}/\Delta g_{\perp}$ also indicates that the octahedral symmetry is reduced when Na_2O is replaced

by Bi_2O_3. The decrease in the value of P with increasing mol% of Bi_2O_3 indicates that the average radius of the unpaired electron in vanadium increases and so its interaction with the nucleus decreases, which is consistent with the decrease in the values of $|A'_\parallel|$ and $|A'_\perp|$.

Theoretical optical basicity serves in the first approximation as a measure [23] of the ability of oxygen to donate a negative charge to the glasses. In other words, the optical basicity reflects the Lewis basicity of oxide glasses. As the ability of the equatorial ligands to donate the electron (i.e. Lewis basicity) decreases, σ bondings between V^{4+} and the ligands reduces [24]. This reduction, in turn, increases the positive charge on V^{4+} and increases the π bondings between V^{4+} and vanadyl oxygen. This increase, decreases the bond length of V^{4+}-vanadyl oxygen. Consequently, the tetragonal nature of the $V^{4+}O_6$ complex is enhanced. In the present glass system, the theoretical optical basicity, Λ_{th}, decreases when M_2O (M = Li or Na) is replaced by Bi_2O_3. This decrease in Λ_{th} predicts that the tetragonal distortion should increase with increase in the ratio Bi_2O_3:M_2O (M = Li, Na). Therefore in $Bi_2O_3 \cdot Na_2O \cdot B_2O_3$ glasses the experimental findings are in accordance with the variation in Λ_{th}, whereas in case of $Bi_2O_3 \cdot Li_2O \cdot B_2O_3$ glasses the SHP are independent of Λ_{th}.

4.2. Optical transmission

$(1 - \alpha^2)$ gives an indication of the effect of σ bonding between vanadium and equatorial ligands, while $(1 - \gamma^2)$ indicates the effect of π bonding with the vanadyl oxygen. Table 2 shows that the values of α^2 vary within experimental error (as the variation in $g_\parallel$ is within the experimental error) whereas the values of γ^2 show a maxima for $x = 6$ mol% in $Bi_2O_3 \cdot Li_2O \cdot B_2O_3$ samples. This indicates that the covalency is minimum for this glass sample, which is in consistence with the EPR results.

Table 4 shows the values of α^2 and γ^2 for $Bi_2O_3 \cdot Na_2O \cdot B_2O_3$ glasses. It is observed that the variation in α^2 is within experimental error because $g_\parallel$ values are also within experimental error, whereas γ^2 decreases with increase in Bi_2O_3:Na_2O ratio. This indicates that the covalency of the vanadium oxygen bonds increase with Bi_2O_3:Na_2O ratio. This indication is consistence with the EPR results.

4.3. DC conductivity

Several models such as the weak electrolyte model [25, 26], the random site model [27], the dynamic structural model [28], the diffusion pathway model [29], the cluster model [30], the cluster-bypass model [31], have been proposed to explain the ion transport in glasses. The ionic conductivity of a solid can be simply expressed as

$$\sigma = Nez\mu, \tag{14}$$

where N is the density of the mobile ions of charge ez and of mobility μ. Thus the exponential variation of conductivity σ

with alkali content, observed in Figs. 3 and 4 may be due to concentration dependence of the mobile carrier density N and because of variation of mobility μ. In the glass samples under study, the total density of alkali ions is known but the fraction of these, which are mobile and contribute to the measured conductivity, is unknown. In general, both N and μ might be expected to be composition or structure dependent. Since the vanadium ions in these glasses may exist in more than one-valence states, e.g. V^{4+} and V^{5+}, conduction could also take place by the transfer of electrons from low to high valence states. Decrease in the conductivity with time reveals that the electrical conductivity is mainly due to alkali ions and it may have only a small contribution of electronic conductivity. Electronic conductivity due to hopping of electrons between V^{4+} and V^{5+} does not play an important part in total conductivity in the present glass system. From Figs. 3–5 it is observed that a suitable way for interpretation of the results may be decrease in the mobility of the alkali ions with increase in the mol% of Bi_2O_3 and decrease in the mobile ion concentration with decrease in mol% of M_2O (M = Li, Na). Abid et al. [32,33] has explained the DC conductivity of alkali lead phosphate glasses on the basis of similar arguments. The decrease in conductivity on the replacement of Li_2O by Na_2O can be explained on the basis that the Na^+ ions are heavier than Li^+ ions.

5. Conclusions

1. V^{4+} ions in these samples exist as VO^{2+} ions in octahedral coordination with a tetragonal compression and belong to C_{4V} symmetry.
2. In $x Bi_2O_3 \cdot (30 - x)Li_2O \cdot 70B_2O_3$ glass samples, for $x \le 6$ mol%, the octahedral symmetry is improved at V^{4+} site and there is decrease in tetragonality of the $V^{4+}O_6$ complex. However, for $6 < x \le 15$ mol%, octahedral symmetry is reduced at V^{4+} ion and the tetragonality of the $V^{4+}O_6$ complex increases.
3. In $x Bi_2O_3 \cdot (30 - x)Na_2O \cdot 70B_2O_3$ glass samples, for increasing x, the octahedral symmetry is reduced at V^{4+} ion site and the tetragonality of $V^{4+}O_6$ complex increases.
4. Increase in the Bi_2O_3:M_2O (M = Li, Na) ratio results in an expansion of the $3d_{xy}$ orbit of unpaired electron in the vanadium ion.
5. In $x Bi_2O_3 \cdot (30 - x)Li_2O \cdot 70B_2O_3$ glass samples, the spin Hamiltonian parameters (SHP) are independent of theoretical optical basicity, Λ_{th}. For $x Bi_2O_3 \cdot (30 - x)Na_2O \cdot 70B_2O_3$ glass samples, the decrease in Λ_{th} is in agreement with the SHP.
6. The values of the molecular orbital coefficients, α^2 and γ^2, indicate that for $x Bi_2O_3 \cdot (30 - x)Li_2O \cdot 70B_2O_3$ samples, covalency is minimum at $x = 6$ mol%, whereas for $x Bi_2O_3 \cdot (30 - x)Na_2O \cdot 70B_2O_3$ samples covalency

increases with increase in Bi_2O_3:Na_2O ratio. These observations are in consonance with the EPR results.

7. The DC conductivity increases with increase in temperature. This increase is about 100 times when the temperature is raised from 423 to 523 K.

8. The DC conductivity decreases and the activation energy increases with increase in Bi_2O_3:M_2O (M = Li, Na) ratio.

Acknowledgements

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