Effect of TiO2 on electron paramagnetic resonance, optical transmission and dc conductivity of vanadyl doped sodium borate glasses

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Effect of TiO$_2$ on electron paramagnetic resonance, optical transmission and dc conductivity of vanadyl doped sodium borate glasses

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Abstract

Glass systems with composition xTiO$_2$·(30 − x)Na$_2$O·70B$_2$O$_3$ (series I) and xTiO$_2$·(70 − x)B$_2$O$_3$·30Na$_2$O (series II) containing 2 mol% V$_2$O$_5$ have been prepared ($0 \leq x \leq 7$, mol%) by normal melt-quenching. The electron paramagnetic resonance (EPR) spectra of VO^{2+} ions have been recorded in the X-band (∼9.13 GHz) at room temperature. Spin Hamiltonian parameters, $g_{||}$, $g_{\perp}$, $A_{||}$, $A_{\perp}$, the dipolar hyperfine coupling parameter (P) and the Fermi contact interaction parameter (K) have been calculated. The increase in $\Delta g_{||}/\Delta g_{\perp}$ with increase in TiO$_2$ content in series I shows that the octahedral symmetry of V^{4+}O$_6$ complex is reduced, whereas in series II the octahedral symmetry is improved with increase in x. The decrease in P, in both the series, indicates that the 3d$_{xy}$ orbit expands with increase in mol% of TiO$_2$. The molecular orbital coefficients, α^2 and γ^2 have been calculated by recording the optical transmission spectra in the range 500–850 nm. α^2 and γ^2 increase with increase in x in both the series, which indicates that, the covalency of the vanadium oxygen bonds decreases. The dc conductivity σ, decreases and activation energy, W increases with increase in TiO$_2$:Na$_2$O ratio whereas with increase in TiO$_2$:B$_2$O$_3$ ratio the variation in σ and W is within experimental error.
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Keywords: EPR; Vanadyl ion; Borate glasses; Ionic conduction; Optical properties

1. Introduction

Structural studies of binary borate glasses of various compositions have been carried out using electron paramagnetic resonance (EPR) spectroscopy of incorporated transition metal (TM) ions [1–7]. The TM ions can be used to probe the glass structure, because their outer d-electron orbital functions have rather broad radial distributions and their response to surrounding cations are very sensitive [8]. Further, it has been well established [9–11] that the alkali borate glasses can be used as solid electrolytes. These glassy electrolytes are of particular importance because of their inherent advantages such as isotropic conductivity, ease of preparation, better thermal stability, and the large available composition ranges that make them potential candidate for technological applications. It has been observed [12] that in

Ti–Ba borate glasses, TiO$_2$ acts as glass former and it gives a more polymerised structure and increases the glass stability with respect to devitrification. It has been shown that [13] Ti^{4+} is the preferred valence state in most of the oxide glasses containing TiO$_2$, which are melted under normal conditions and Ti^{3+} is facilitated by glass preparation under extremely reducing conditions. The aim of the present work is to investigate the influence of TiO$_2$ content on the EPR, optical transmission and dc conductivity of vanadyl doped Na$_2$O·B$_2$O$_3$ glasses.

2. Experimental

The starting materials used were the analar grade reagents of Na$_2$CO$_3$, TiO$_2$ and H$_3$BO$_3$ with 2.0 mol% V$_2$O$_5$ added to each batch. Each batch was melted at 1323 K in a porcelain crucible for half an hour in an electric muffle furnace in air. The melt was poured onto one carbon plate and pressed with another quickly. The batch composition (in mol%) is

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Table 1
Spin Hamiltonian parameters[a] of VO^{2+} at room temperature and Λ_{th} in $xTiO_2 \cdot (30-x)Na_2O \cdot 70B_2O_3$ glasses

Glass no.	x (mol%)	V_2O_5 (mol%)	$g_{\parallel}$ (± 0.001)	$g_{\perp}$ (± 0.000)	$\lvert A_{\parallel}\rvert$ ($\times 10^{-4}$ cm^{-1}) (± 1.0)	$\lvert A_{\perp}\rvert$ ($\times 10^{-4}$ cm^{-1}) (± 1.0)	Λ_{th}
1	0	2	1.9376	1.9746	166.89	60.38	0.5134
2	2	2	1.9347	1.9734	166.65	60.35	0.5094
3	5	2	1.9342	1.9734	167.14	60.81	0.5037
4	7	2	1.9336	1.9734	167.00	61.27	0.4999

[a] $A_{\parallel}$ and $A_{\perp}$ are negative.

shown in Tables 1 and 3. The EPR spectra of crushed glasses were recorded at room temperature on a Varian E-112, reflection type spectrometer operating in the X-band ($\nu \sim$ 9.13 GHz) with an applied magnetic field modulation of 100 kHz. The resonance line of DPPH with $g = 2.0036$ was used as a field marker. The optical transmission spectra of the as-prepared samples were recorded at room temperature using a Perkin-Elmer UV-Vis spectrometer (Lambda 20) in the wavelength range 500–850 nm. For dc conductivity measurements, as-prepared samples were grinded and finely polished to attain uniform thickness. The silver paint electrodes were pasted on both faces of the polished samples

and the measurements were made by the standard method in the temperature range 373–523 K, first by increasing the temperature and then by decreasing it. A constant voltage of 10 V was applied across the sample and circulating current was measured using Keithley 617 programmable electrometer/source.

3. Results

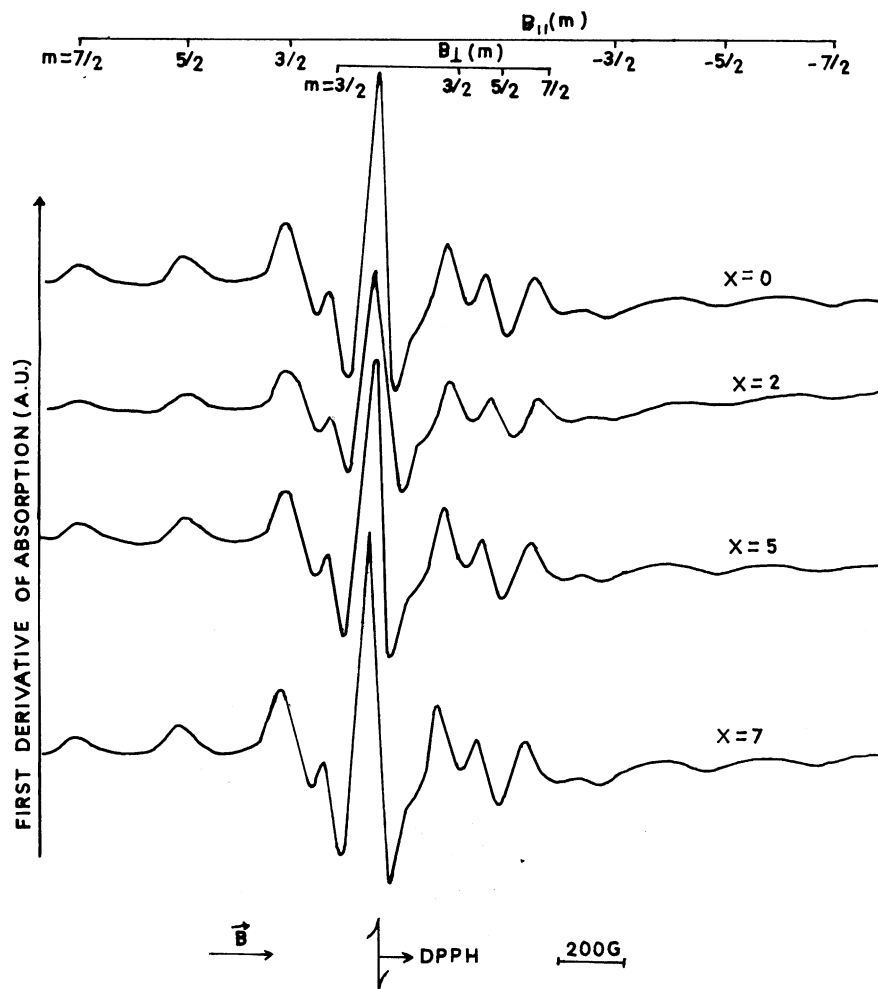Fig. 1 shows the EPR spectra of the VO^{2+} ions in glass nos. 5–8 at room temperature. These spectra show feature

Fig. 1. The EPR spectra of VO^{2+} ions in $xTiO_2 \cdot (70-x)B_2O_3 \cdot 30Na_2O$ glasses in the X-band ($\nu \sim 9.13$ GHz) at room temperature.

which is due to hyperfine interaction of a single unpaired electron with a ^{51}V nucleus whose nuclear spin (I) is 7/2. These spectra were analysed by assuming [5–7] that vanadium is present as a vanadyl ion in a ligand field of C_{4V} symmetry. The spin Hamiltonian used is of the form [2]

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

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:

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

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

where m is the magnetic quantum number of the vanadium nucleus, $B_{\parallel}(0) = h\nu/g_{\parallel}\beta$ and $B_{\perp}(0) = h\nu/g_{\perp}\beta$, where h is the Planck constant, ν 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 (SHP) of the VO^{2+} ions determined by using Eqs. (2) and (3) for the EPR spectra of all the samples are presented 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, $P = 2\gamma\beta\beta_N \langle r^{-3} \rangle$, and the Fermi contact interaction term, K, are evaluated using the following expressions developed by Kivelson and Lee [14]:

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

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

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 [15,16]. Both $A_{\parallel}$ and $A_{\perp}$ are found to be negative by the method proposed by Muncaster

and Parke [17]. 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 polarisation of the inner s-electrons as a result of an interaction with the unpaired d-electrons [18]. The estimate of this polarisation was made by Heine [18] and the contribution to the hyperfine coupling due to the term $-PK$ is included. For transition metal ions, K is found to be positive [16]. From the molecular orbital theory, it can also be shown [15] 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) can be rewritten in the following way:

$$A_{\parallel} = -PK - P[(\tfrac{4}{7}) - \Delta g_{\parallel} - (\tfrac{3}{7})\Delta g_{\perp}] = -PK + A_{\parallel}' \tag{6}$$

$$A_{\perp} = -PK + P[(\tfrac{2}{7}) + (\tfrac{11}{14})\Delta g_{\perp}] = -PK + A_{\perp}' \tag{7}$$

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 [15], are also included in these Tables.

Theoretical optical basicity, Λ_{th}, has been calculated [19] by using the expression

$$\Lambda_{th} = \sum_i \frac{Z_i r_i}{2\gamma_i} \tag{8}$$

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

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

where x_i is the Pauling electronegativity [20] of the cation i. The calculated values of Λ_{th} of all the samples are given in Tables 1 and 3.

3.1. Optical transmission

In the present study, only two transmission bands are observed in all the glass samples. The TiO$_2$-containing samples neither have a transmission band around 500 nm due to the $^2T_{2g} \rightarrow {}^2E_g$ transition of Ti^{3+} ions in octahedral sites [21], nor bands around 540 and 660 nm due to the $^2B_{2g} \rightarrow {}^2B_{1g}$ and $^2B_{2g} \rightarrow {}^2A_{1g}$ transitions of Ti^{3+} ions in distorted octahedral sites [22]. Therefore, Ti ions in the present glass

Table 2
P, K, $|A_{\parallel}'|$, $|A_{\perp}'|$, $\Delta g_{\parallel}/\Delta g_{\perp}$, α^2 and γ^2 of VO^{2+} in xTiO$_2$·(30 − x)Na$_2$O·70B$_2$O$_3$ glasses at room temperature

Glass no.	P ($\times 10^{-4}$ cm^{-1})	K	$|A_{\parallel}'|$ ($\times 10^{-4}$ cm^{-1})	$|A_{\perp}'|$ ($\times 10^{-4}$ cm^{-1})	$\Delta g_{\parallel}/\Delta g_{\perp}$	α^2	γ^2
1	116.8	0.7809	75.69	30.83	2.3360	0.579	0.716
2	116.3	0.7821	75.73	30.58	2.3388	0.605	0.747
3	116.2	0.7862	75.77	30.57	2.3584	0.610	0.747
4	115,5	0.7935	75.36	30.38	2.3780	0.615	0.747

Table 3
Spin Hamiltonian parameters[a] of VO^{2+} at room temperature and Λ_{th} in $xTiO_2 \cdot (70 - x)B_2O_3 \cdot 30Na_2O$ glasses

Glass no.	x (mol%)	V_2O_5 (mol%)	$g_{\parallel}$ (± 0.001)	$g_{\perp}$ (± 0.001)	$|A_{\parallel}|$ ($\times 10^{-4}$ cm^{-1}) (± 1.0)	$|A_{\perp}|$ ($\times 10^{-4}$ cm^{-1}) (± 1.0)	Λ_{th}
5[b]	0	2	1.9376	1.9746	166.89	60.38	0.5134
6	2	2	1.9370	1.9740	166.75	60.36	0.5170
7	5	2	1.9370	1.9734	165.94	59.70	0.5226
8	7	2	1.9370	1.9734	165.85	59.70	0.5263

[a] $A_{\parallel}$ and $A_{\perp}$ are negative.
[b] Glass nos. 1 and 5 have same composition.

system were concluded to be present as Ti^{4+} ions. Fig. 2 shows optical transmission spectra of sample nos. 1 and 4. The two transmission bands at 560 and 776 nm were observed. These two bands are typical for VO^{2+} and can be assigned to $b_2 \rightarrow b_1^*$ and $b_2 \rightarrow e_{\Pi}^*$ transitions, respectively. The values of $g_{\parallel}$ and $g_{\perp}$ are related to bonding parameters by the following equations [15]:

$$\gamma^2 = \frac{[1 - (g_{\perp}/g_e)]E_1}{\lambda \beta^2} \tag{10}$$

$$\alpha^2 = \frac{[1 - (g_{\parallel}/g_e)]E_2}{4\lambda \beta^2} \tag{11}$$

where E_1 and E_2 are the energies of transitions $b_2 \rightarrow e_{\Pi}^*$ 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 one for many glasses containing VO^{2+} [19]. λ is the spin–orbit coupling constant and is equal to 249 cm^{-1} [17]. The expressions $(1-\alpha^2)$ and $(1-\gamma^2)$ are the covalency rates. Using Eqs. (10) and (11), the values of γ^2 and α^2 were calculated and are given in Tables 2 and 4.
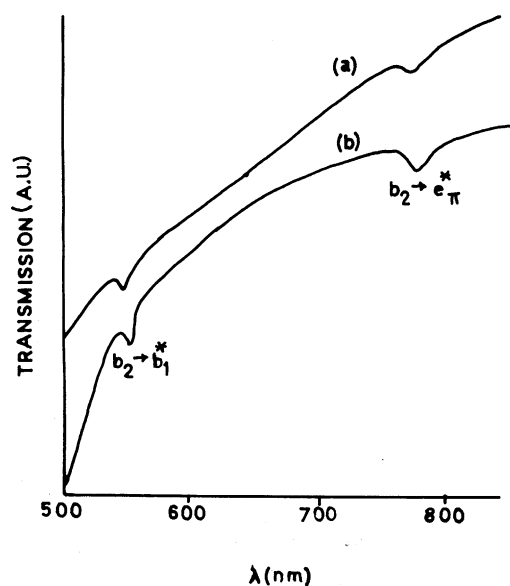
3.2. dc Conductivity

The temperature dependence of the conductivity in the temperature range 373–523 K is shown in Figs. 3 and 4 for $xTiO_2 \cdot (30 - x)Na_2O \cdot 70B_2O_3$ and $xTiO_2 \cdot (70 - x)B_2O_3 \cdot 30Na_2O$ glass systems, respectively. The temperature dependence of the dc conductivity obeys the well-known Arrhenius formula:

$$\sigma = \sigma_0 \exp\left(\frac{-W}{kT}\right) \tag{12}$$

where W is the activation energy for conduction and the pre-exponential factor, σ_0, contains several constants including the vibrational frequency of the mobile ion [23]. The values of W, $\log \sigma_0$ and σ at 373 and 523 K are shown in Tables 5 and 6. From Fig. 3 and Table 5, it is observed that the dc conductivity decreases and activation energy, W increases with increase in TiO_2:Na_2O ratio. On the other hand, when TiO_2 replaces B_2O_3, keeping Na_2O constant, it is observed from Fig. 4 and Table 6 that the variation in dc conductivity and activation energy is within experimental error.
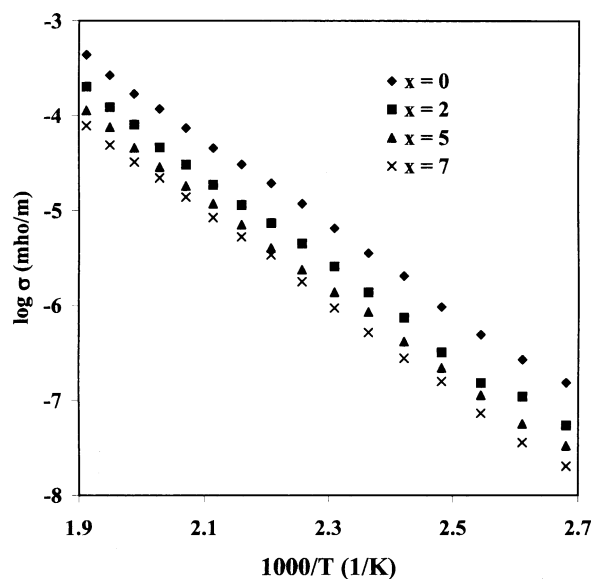

Fig. 2. The optical transmission spectra of VO^{2+} ions in $xTiO_2 \cdot (30 - x)Na_2O \cdot 70B_2O_3$ glasses for (a) $x = 0$ and (b) $x = 7$ mol% at room temperature.

Fig. 3. Variation of $\log \sigma$ vs. $10^3 T^{-1}$ for $xTiO_2 \cdot (30 - x)Na_2O \cdot 70B_2O_3$ glasses.

Table 4
P, K, $|A'_\parallel|$, $|A'_\perp|$, $\Delta g_\parallel/\Delta g_\perp$, α^2 and γ^2 of VO^{2+} in $x\mathrm{TiO_2 \cdot (70-x)B_2O_3 \cdot 30Na_2O}$ glasses at room temperature

Glass no.	P ($\times 10^{-4}$ cm^{-1})	K ($\times 10^{-4}$ cm^{-1})	$|A'_\parallel|$ ($\times 10^{-4}$ cm^{-1})	$|A'_\perp|$	$\Delta g_\parallel/\Delta g_\perp$	α^2	γ^2
5[a]	116.8	0.7809	75.69	30.83	2.3360	0.579	0.716
6	116.6	0.7811	75.67	30.72	2.3074	0.585	0.731
7	116.5	0.7755	75.61	30.63	2.2603	0.585	0.747
8	116.4	0.7759	75.54	30.61	2.2603	0.585	0.747

[a] Glass nos. 1 and 5 have same composition.

Table 5
dc conductivity σ, $\log \sigma_0$ and activation energy, W of $x\mathrm{TiO_2 \cdot (30-x)Na_2O \cdot 70B_2O_3}$ glasses

Glass no.	x (mol%)	V_2O_5 (mol%)	σ_{at373K} (Ω^{-1} m^{-1})	σ_{at523K} (Ω^{-1} m^{-1})	$\log \sigma_0$ (Ω^{-1} m^{-1})	W (eV)
1	0	2	1.53×10^{-7}	4.38×10^{-4}	5.25	0.90
2	2	2	5.43×10^{-8}	2.03×10^{-4}	4.90	0.92
3	5	2	3.33×10^{-8}	1.13×10^{-4}	5.18	0.93
4	7	2	2.03×10^{-8}	7.78×10^{-5}	4.92	0.94

Table 6
dc conductivity σ, $\log \sigma_0$ and activation energy, W of $x\mathrm{TiO_2 . (70-x)B_2O_3 \cdot 30Na_2O}$ glasses

Glass no.	x (mol%)	V_2O_5 (mol%)	σ_{at373K} (Ω^{-1} m^{-1})	σ_{at523K} (Ω^{-1} m^{-1})	$\log \sigma_0$ (Ω^{-1} m^{-1})	W (eV)
5[a]	0	2	1.53×10^{-7}	4.38×10^{-4}	5.25	0.90
6	2	2	1.41×10^{-7}	4.21×10^{-4}	5.30	0.89
7	5	2	1.68×10^{-7}	4.50×10^{-4}	5.40	0.89
8	7	2	1.55×10^{-7}	4.32×10^{-4}	5.48	0.90

[a] Glass nos. 1 and 5 have same composition.
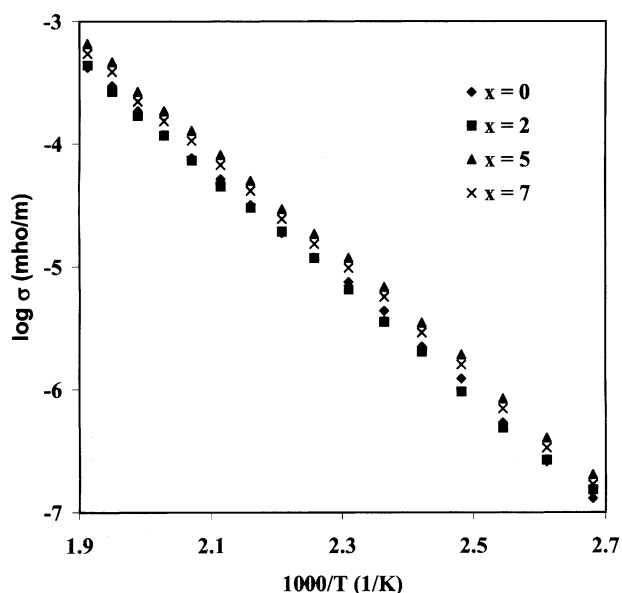
Fig. 4. Variation of $\log \sigma$ vs. $10^3 \, T^{-1}$ for $x\mathrm{TiO_2 \cdot (70-x)B_2O_3 \cdot 30Na_2O}$ glasses.

4. Discussion

4.1. EPR

In oxide glasses containing vanadyl ion, although the V^{4+} ion is usually six co-ordinated, its local symmetry is gen- erally a distorted octahedron of oxygen ions, i.e., the bond length between vanadium and the vanadyl oxygen is extraor- dinarily short compared with its bond length with other lig- ands. Hecht and Johnston [2] studied extensively the EPR and optical spectra of V^{4+} ions in soda boric-oxide glasses and observed that the vanadyl ion exists in the sample with one of the two possible symmetries, i.e., either three-fold or four-fold 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 the present samples under study exist as VO^{2+} ions in octahedral co-ordination with a tetragonal compression and belong to C_{4V} symmetry.

Tables 1 and 2 show that the variation in the values of $|A_\parallel|$ and $|A'_\parallel|$ is within experimental error when Na_2O is replaced by TiO_2, whereas the values of $g_\parallel$, $g_\perp$, P, $|A'_\perp|$ decrease and the values of $|A_\perp|$, K and $\Delta g_\parallel/\Delta g_\perp$ increase. As suggested by Kivelson and Lee [14], we assume [24–26] that the increase in the value of K with increase in TiO_2:Na_2O ratio is due to an increase 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 $\Delta g_\parallel/\Delta g_\perp$ also shows that the octahedral symmetry is reduced when Na_2O is replaced by TiO_2. The decrease of the anisotropic contribution (i.e., $|A'_\perp|$) of the $3d_{xy}$-electron to the hyperfine splitting is brought about by increased [15] 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 electron with the vanadium nucleus. Decrease in the value of P also supports the argument that the $3d_{xy}$ orbit expands with increase in TiO_2:Na_2O ratio.

Theoretical optical basicity, Λ_{th}, serves in the first approximation as a measure [27] of the ability of oxygen to donate a negative charge in the glasses. In other words, Λ_{th} reflects the Lewis basicity of the oxide glasses. As the ability of the equatorial ligands to donate the electron (i.e., Lewis basicity) decreases, σ bonding between V^{4+} and the ligands reduces [28]. This reduction, in turn, increases the positive charge on V^{4+} and increases the π bonding between V^{4+} and vanadyl oxygen. This increase, in turn, decreases the bond length of V^{4+}-(vanadyl oxygen). Consequently, the tetragonal nature of the $V^{4+}O_6$ complex is enhanced. From Table 1, it is observed that the theoretical optical basicity, Λ_{th}, of the host glass decreases when Na_2O is replaced by TiO_2. This decrease in Λ_{th}, predicts that the tetragonal distortion should increase with increase in TiO_2:Na_2O ratio, which is in agreement with experimental findings.

It is evident from Tables 3 and 4 that $g_{||}$, $g_{\perp}$, $|A_{||}|$, $|A_{\perp}|$, P, K, $|A'_{||}|$ $|A'_{\perp}|$ and $\Delta g_{||}/\Delta g_{\perp}$ decrease when B_2O_3 is replaced by TiO_2 keeping mol of Na_2O constant. Decrease in the value of K with increase in TiO_2:B_2O_3 ratio is due to the decrease [24–26] in the tetragonal nature of the $V^{4+}O_6$ complex because of a strongly bonded oxygen atom at the V^{4+} ion in the site opposite to the vanadyl oxygen. Decrease in the value of $\Delta g_{||}/\Delta g_{\perp}$ also supports the argument that the octahedral symmetry is improved when B_2O_3 is replaced by TiO_2. The decrease in the value of P with increase in TiO_2:B_2O_3 ratio, 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 value of $|A'_{||}|$ and $|A'_{\perp}|$. Table 3 shows that, Λ_{th} increases with increase in TiO_2:B_2O_3 ratio. This variation predicts that the tetragonal distortion should decrease with increase in TiO_2:B_2O_3 ratio which is in accordance with the EPR results.

4.2. Optical transmission

The expression $(1 - \alpha^2)$ gives an indication of the effect of the σ bonding between vanadium atom and the equatorial ligands, while the expression $(1 - \gamma^2)$ indicates the influence of the π bondings with the vanadyl oxygen. Table 2 shows that the values of α^2 and γ^2 increase with increase in TiO_2:Na_2O ratio, which indicates that the covalency of the vanadium oxygen bonds decreases when Na_2O is replaced by TiO_2, keeping B_2O_3 constant [15]. Table 4 shows that the values of α^2 and γ^2 also increase with increase in TiO_2:B_2O_3 ratio, which indicates that the covalency of the vanadium oxygen bonds decreases [15]. These findings based on optical transmission are in agreement with the EPR results.

4.3. dc Conductivity

The ionic conductivity of a solid can be expressed as [29]

$$\sigma = Nez\mu \tag{13}$$

where N is the density of mobile ions of charge ez and of mobility μ. The conductivity can vary with the variation in N and/or μ. The ionic mobility, μ, depends on the atomic structure which dictates the possible pathways available for migration [9]. In the glass samples under study, the total density of Na^+ 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 but the decrease in conductivity with time reveals that the electrical conductivity is mainly due to Na^+ ions and it may have only a small contribution of electronic conductivity. Further, in the present TiO_2-containing glasses, Ti is present as Ti^{4+} ions, therefore, there is no possibility that the conduction may occur by hopping of electron from low to high valence states of Ti (Ti^{3+} and Ti^{4+}). Therefore, in the present study, the conduction mechanism is mainly ionic in nature. From Fig. 3 and Table 5, it is observed that the decrease in σ and increase in W, may be due to decrease in number of mobile Na^+ ions and decrease in their mobility with increasing TiO_2:Na_2O ratio. In other words, TiO_2 shows 'blocking effect' on the migration of mobile Na^+ ions. Similar arguments were considered by other authors for the decrease in σ when in a binary glass, a third component was added [30,31]. From Fig. 4 and Table 6, it is observed that the variation in σ and W, with increase in TiO_2:B_2O_3 ratio, keeping Na_2O constant, is within experimental error. Therefore, σ is purely dependent on the concentration of mobile Na^+ ions and there is no change in mobility of these ions. Therefore, it may be assumed [32] that Ti ions are introduced as network formers in the form of Ti^{4+} and not as network modifiers in $xTiO_2 \cdot (70 - x)B_2O_3 \cdot 30Na_2O$ glass system.

5. Conclusions

V^{4+} ions in these samples exist as VO^{2+} ions in octahedral co-ordination with a tetragonal compression and belong to C_{4V} symmetry. There is an increase in the tetragonal nature of $V^{4+}O_6$ complex with increase in TiO_2:Na_2O ratio whereas the tetragonal nature of $V^{4+}O_6$ complex decrease with increase in TiO_2:B_2O_3. The $3d_{xy}$ orbit of unpaired electron in the VO^{2+} ion expands with increase in TiO_2 content, in both the glass series. The values of the molecular orbital coefficients indicate that the degree of covalency of the vanadium oxygen bonds decreases with increase in TiO_2 content, in both the glass systems. The dc conductivity, σ increases with increase in temperature. This

increase is about 1000 times when the temperature is raised from 373 to 523 K. There is no contribution of Ti ions in the electrical conduction. The dc conductivity decreases and activation energy increases with increase in $TiO_2:Na_2O$ ratio in $xTiO_2 \cdot (70 - x)B_2O_3 \cdot 30Na_2O$ glass system, whereas the variations in σ and W are within experimental error with increase in $TiO_2:B_2O_3$ ratio in $xTiO_2 \cdot (70 - x)B_2O_3 \cdot 30Na_2O$ glass system.

Acknowledgements

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