

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/248261161>

# Effect of $\text{Bi}_2\text{O}_3$ on electron paramagnetic resonance, optical transmission and conductivity in vanadyl-doped $\text{Bi}_2\text{O}_3 \cdot \text{K}_2\text{O} \cdot \text{B}_2\text{O}_3$ glasses

ARTICLE *in* MATERIALS CHEMISTRY AND PHYSICS · MAY 2004

Impact Factor: 2.26 · DOI: 10.1016/j.matchemphys.2004.01.017

---

CITATIONS

13

---

READS

42

5 AUTHORS, INCLUDING:



Satish Khasa

Deenbandhu Chhotu Ram University of Sci...

45 PUBLICATIONS 249 CITATIONS

SEE PROFILE

# Effect of $\text{Bi}_2\text{O}_3$ on electron paramagnetic resonance, optical transmission and conductivity in vanadyl-doped $\text{Bi}_2\text{O}_3 \cdot \text{K}_2\text{O} \cdot \text{B}_2\text{O}_3$ glasses

A. Agarwal<sup>a,\*</sup>, V.P. Seth<sup>b</sup>, P.S. Gahlot<sup>b</sup>, S. Khasa<sup>c</sup>, P. Chand<sup>d</sup>

<sup>a</sup> Department of Applied Physics, G.J. University, Hisar 125001, India

<sup>b</sup> Department of Physics, M.D. University, Rohtak 124001, India

<sup>c</sup> Department of Physics, Government College, Bahadurgarh 124507, India

<sup>d</sup> Department of Physics, Indian Institute of Technology, Kanpur, India

Received 11 June 2003; received in revised form 18 January 2004; accepted 22 January 2004

## Abstract

Glasses with composition  $x\text{Bi}_2\text{O}_3 \cdot (30 - x)\text{K}_2\text{O} \cdot 70\text{B}_2\text{O}_3$  doped with 2 mol% of  $\text{V}_2\text{O}_5$  have been prepared over the range  $0 \leq x \leq 15$  (in mol%). The electron paramagnetic resonance spectra of  $\text{VO}^{2+}$  in these glasses have been recorded in the X-band ( $\approx 9.3$  GHz) at room temperature. The spin Hamiltonian parameters, dipolar hyperfine coupling parameter and Fermi contact interaction parameter have been calculated. It is observed that, with increase in  $\text{Bi}_2\text{O}_3 \cdot \text{K}_2\text{O}$  ratio, tetragonal distortion of the  $\text{V}^{4+}\text{O}_6$  complex increases and there is an expansion of the  $3d_{xy}$  orbit of unpaired electron in the vanadium ion. The values of theoretical optical basicity have also been reported. The molecular orbital coefficients have been calculated by recording the optical transmission spectra in the wavelength range 500–850 nm. The direct-current electrical conductivity,  $\sigma$ , has been measured in the temperature range 443–523 K.  $\sigma$  decreases with increase in  $\text{Bi}_2\text{O}_3 \cdot \text{K}_2\text{O}$  ratio because of the decrease in the mobility and number of mobile  $\text{K}^+$  ions and there is no electronic contribution to the conductivity by  $\text{Bi}_2\text{O}_3$ .

© 2004 Elsevier B.V. All rights reserved.

**Keywords:** Electron paramagnetic resonance; Oxide glasses; Electrical conductivity; Vanadyl ion

## 1. Introduction

Electron paramagnetic resonance (EPR) spectroscopy is an experimental technique to obtain detailed information on some of the structural and dynamic phenomena of a material and to identify site symmetry around transition metal ions in glasses [1,2]. The transition metal ions can be used to probe the glass structure, because their outer d electron orbital functions have rather broad radial distributions and their responses to surroundings cations are very sensitive [3]. The glasses doped with transition metal ions have attracted a great deal of attention because of their potential applications in the development of new tunable solid-state lasers, solar-energy converters, and fiber-optic communication devices [4].

In the present study, the vanadyl ion ( $\text{VO}^{2+}$ ) has been used as a spectroscopic probe for characterization of glasses because their EPR spectra are rich in hyperfine structure due

to the  $^{51}\text{V}$  nucleus (nuclear spin  $I = \frac{7}{2}$ ) and is easily observable at room temperature [5–11]. It has been well established that alkali borate glasses can be used as solid electrolytes [12–14]. These glassy electrolytes are of significance because of their inherent advantages such as isotropic conductivity, ease of preparation, better thermal stability and the large available composition ranges. It has been shown that the addition of  $\text{Bi}_2\text{O}_3$  leads to an improvement in the chemical durability and thermal stability of oxide glasses [15]. The aim of the present work is to investigate the effect of  $\text{Bi}_2\text{O}_3$  on the EPR, optical transmission and direct-current (DC) conductivity in vanadyl-doped potassium borate glasses.

## 2. Experimental

The analytical grade reagents of  $\text{K}_2\text{CO}_3$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  were used as starting materials. The glass compositions in mol% are shown in Table 1. Each batch was melted at 1273 K in a porcelain crucible for 0.5 h in an electric muffle furnace. The melt was poured onto one carbon plate and pressed with another very quickly. The first-derivative

\* Corresponding author. Tel.: +91-1662-277081;

fax: +91-1662-276240.

E-mail address: [aagju@yahoo.com](mailto:aagju@yahoo.com) (A. Agarwal).

Table 1  
Spin Hamiltonian parameters<sup>a</sup> of VO<sup>2+</sup> at room temperature and  $\Lambda_{th}$  in  $x\text{Bi}_2\text{O}_3 \cdot (30 - x)\text{K}_2\text{O} \cdot 70\text{B}_2\text{O}_3$  glasses

Glass number	$x$ (mol%)	$\text{V}_2\text{O}_5$ (mol%)	$g_{  }$ ( $\pm 0.001$ )	$g_{\perp}$ ( $\pm 0.001$ )	$ A_{  } $ ( $\times 10^{-4} \text{ cm}^{-1}$ ) ( $\pm 1.0$ )	$ A_{\perp} $ ( $\times 10^{-4} \text{ cm}^{-1}$ ) ( $\pm 1.0$ )	$\Lambda_{th}$
1	0	2	1.9437	1.9738	167.97	58.98	0.5400
2	2	2	1.9437	1.9738	167.97	58.98	0.5310
3	4	2	1.9436	1.9738	166.50	58.98	0.5223
4	6	2	1.9429	1.9738	166.45	58.98	0.5139
5	8	2	1.9430	1.9738	166.27	58.98	0.5057
6	10	2	1.9431	1.9739	166.01	58.98	0.4978
7	12	2	1.9424	1.9738	165.95	58.98	0.4901
8	15	2	1.9424	1.9738	165.95	59.16	0.4790

<sup>a</sup>  $A_{||}$  and  $A_{\perp}$  are negative.

EPR spectra were recorded at room temperature (300 K) in the X-band ( $\nu \approx 9.3 \text{ GHz}$ ) on an EPR spectrometer (Varian E-109). The magnetic field was modulated by 100 kHz. Polycrystalline diphenyl picryl hydrazyl with  $g = 2.0036$  was used as a standard for the determination of the spin Hamiltonian parameters. The optical transmission spectra were recorded at room temperature using a Perkin Elmer UV/Vis spectrometer (Lambda 20) in the wavelength range 500–850 nm. To measure the dc conductivity, the glasses were polished on both sides and colloidal silver paint was used as an electrode material. The conductivity was mea-

sured with the help of a Keithley 617 programmable electrometer/source by the standard technique [5].

3. Results

3.1. EPR

Fig. 1 shows the EPR spectra of the VO<sup>2+</sup> in  $x\text{Bi}_2\text{O}_3 \cdot (30 - x)\text{K}_2\text{O} \cdot 70\text{B}_2\text{O}_3$  glasses for  $x = 2, 4, 6$ , and 10 mol% at room temperature. Similar spectra were obtained for other

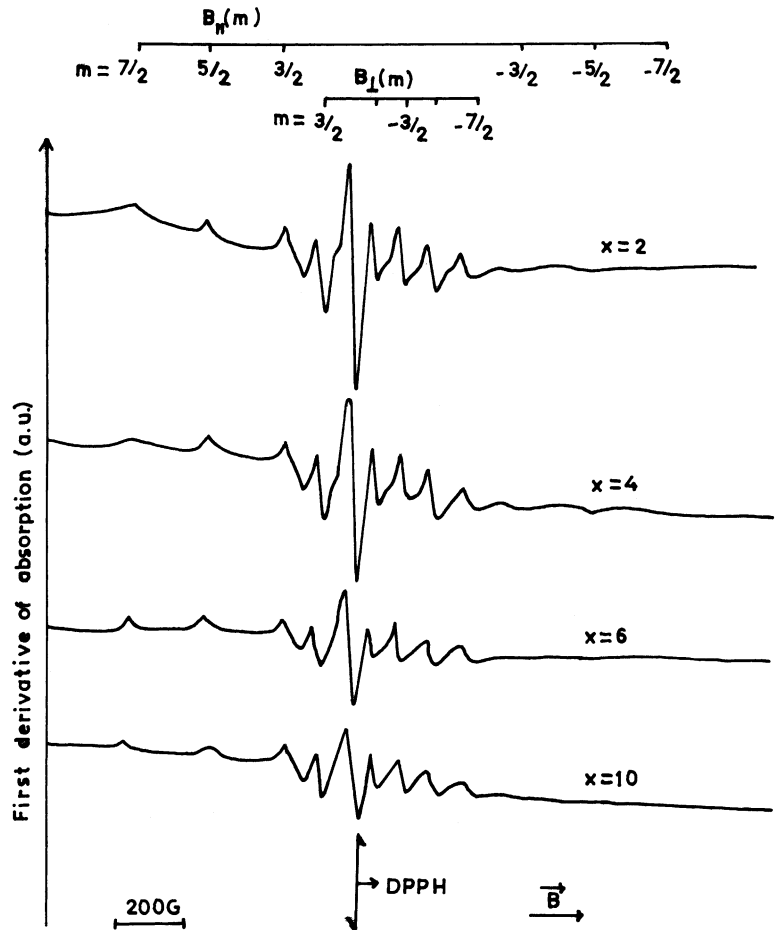


Fig. 1. The EPR spectra of VO<sup>2+</sup> ions in  $x\text{Bi}_2\text{O}_3 \cdot (30 - x)\text{K}_2\text{O} \cdot 70\text{B}_2\text{O}_3$  glasses in the X-band ( $\nu \approx 9.3 \text{ GHz}$ ) at room temperature.

samples. These spectra show a hyperfine structure which is due to a hyperfine interaction of a single unpaired electron with a  $^{51}\text{V}$  nucleus whose nuclear spin is  $\frac{7}{2}$ . Similar EPR spectra of  $\text{VO}^{2+}$  in oxide glasses were obtained by other authors [5–11]. These spectra were analyzed by assuming [8,9] that vanadium is present as a vanadyl ion in a ligand field of  $\text{C}_{4v}$  symmetry. The spin Hamiltonian used is of the form [6]

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

where  $\beta$  is the Bohr magnetron;  $g_{\parallel}$  and  $g_{\perp}$  are the parallel and perpendicular principal components of the  $g$  tensor;  $A_{\parallel}$  and  $A_{\perp}$  the parallel and perpendicular principal components of hyperfine coupling tensor;  $B_x$ ,  $B_y$  and  $B_z$  the components of the magnetic field; and  $S_x$ ,  $S_y$ ,  $S_z$  and  $I_x$ ,  $I_y$ ,  $I_z$  the components of spin operators of the electron and nucleus, respectively. The quadruple and nuclear Zeeman interaction terms have been ignored. The solutions [7] of the spin Hamiltonian (1) are given in Eqs. (2) and (3) for the parallel and perpendicular orientations, respectively:

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

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

where  $m$  is the magnetic quantum number of the vanadium nucleus,  $B_{\parallel}(0) = h\nu/g_{\parallel}\beta$  and  $B_{\perp}(0) = h\nu/g_{\perp}\beta$ . Measurements for the  $B_{\parallel}$  position were taken which correspond to a maximum in the first-derivative curve of the parallel hyperfine structure component for a given  $m$  value, whereas the  $B_{\perp}$  position is enclosed between the first-derivative perpendicular peak and its “zero” [6]. The spin Hamiltonian parameters of the  $\text{VO}^{2+}$  ion determined from Eqs. (2) and (3) for different samples are reported in Table 1. 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 expressions developed by Kivelson and Lee [16]:

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

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

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.  $A_{\parallel}$  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 polarization of the inner s electrons as a result of an interaction with the unpaired d electrons [18]. The estimate of this polarization 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 [19]. From the molecular orbital theory, it can also be shown [20] 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:

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

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

The values of  $P$ ,  $K$ ,  $A'_{\parallel}$  and  $A'_{\perp}$  were calculated and are given in Table 1. The values of  $\Delta g_{\parallel}/\Delta g_{\perp}$ , which measures the tetragonality of the vanadium site [20], are also included in Table 2.

The theoretical optical basicity,  $A_{th}$ , is calculated [21] by using the expression

$$A_{th} = \sum_i \left( \frac{Z_i r_i}{2\gamma_i} \right) \quad (8)$$

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  $\gamma_i$  the basicity moderating parameter.  $\gamma_i$  for the cation is given by

$$\gamma_i = 1.36(x_i - 0.26) \quad (9)$$

where  $x_i$  is the Pauling electronegativity [22]. The theoretical values of optical basicity thus calculated are included in Table 1.

### 3.2. Optical transmission

Fig. 2 shows optical transmission spectra for sample nos. 2 and 4. For all the samples only two transmission bands at 559 and 779 nm were observed. These two transmission

Table 2  
 $P$ ,  $K$ ,  $|A'_{\parallel}|$ ,  $|A'_{\perp}|$ ,  $\Delta g_{\parallel}/\Delta g_{\perp}$ ,  $\alpha^2$  and  $\gamma^2$  of  $\text{VO}^{2+}$  in  $x\text{Bi}_2\text{O}_3 \cdot (30-x)\text{K}_2\text{O} \cdot 70\text{B}_2\text{O}_3$  glasses at room temperature

Glass number	$P$ ( $\times 10^{-4} \text{ cm}^{-1}$ )	$K$	$ A'_{\parallel} $ ( $\times 10^{-4} \text{ cm}^{-1}$ )	$ A'_{\perp} $ ( $\times 10^{-4} \text{ cm}^{-1}$ )	$\Delta g_{\parallel}/\Delta g_{\perp}$	$\alpha^2$	$\gamma^2$
1	119.26	0.758	76.60	31.40	2.0541	0.526	0.734
2	119.26	0.758	76.60	31.40	2.0541	0.526	0.734
3	118.72	0.760	76.26	31.26	2.0641	0.527	0.734
4	118.58	0.761	76.25	31.22	2.0835	0.533	0.734
5	118.40	0.761	76.12	31.18	2.0836	0.532	0.734
6	118.11	0.763	75.92	31.11	2.0838	0.531	0.731
7	117.97	0.763	75.91	31.07	2.1032	0.537	0.734
8	117.75	0.766	75.78	31.00	2.1031	0.537	0.734

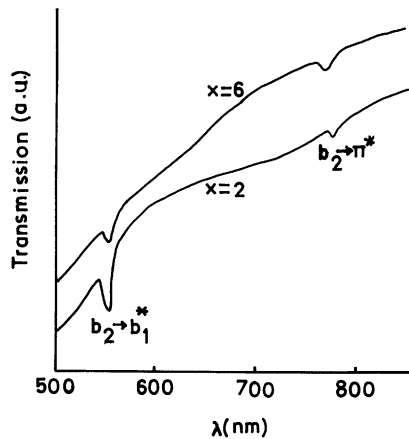


Fig. 2. The optical transmission spectra of  $\text{VO}^{2+}$  ions in  $x\text{Bi}_2\text{O}_3 \cdot (30-x)\text{K}_2\text{O} \cdot 70\text{B}_2\text{O}_3$  glasses for  $x = 2$  and 6 mol% at room temperature.

bands are typical for  $\text{VO}^{2+}$  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 [20]:

$$\alpha^2 = \left[ 1 - \left( \frac{g_{\parallel}}{g_e} \right) \right] \frac{E_2}{4\lambda\beta^2} \quad (10)$$

$$\gamma^2 = \left[ 1 - \left( \frac{g_{\perp}}{g_e} \right) \right] \frac{E_1}{\lambda\beta^2} \quad (11)$$

where  $E_1$  and  $E_2$  are the energy of transitions  $b_2 \rightarrow e_{\pi}^*$  and  $b_2 \rightarrow b_1^*$ , respectively.  $\beta^2$  is a measure of the in-plane  $\pi$ -bonding with the equilateral ligands, which is taken to be equal to 1 for many glasses containing  $\text{VO}^{2+}$  ion [21].  $\lambda$  is the spin-orbit coupling constant and is equal to  $249\text{ cm}^{-1}$  [17]. The expressions  $(1 - \alpha^2)$  and  $(1 - \gamma^2)$  are degrees of covalency. The values of  $\alpha^2$  and  $\gamma^2$  were calculated using Eqs. (10) and (11) and these are included in Table 2.

### 3.3. DC conductivity

The temperature dependence of the DC conductivity in the temperature range 443–523 K is shown in Fig. 3 for  $\text{Bi}_2\text{O}_3 \cdot \text{K}_2\text{O} \cdot \text{B}_2\text{O}_3$  glasses as plots of  $\log \sigma$  versus reciprocal of temperature. The temperature dependence of the conductivity obeys the well-known Arrhenius formula:

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

where  $k$  is the Boltzmann constant,  $T$  the absolute temperature, and  $W$  the activation energy for conduction (average value of the heights of the potential energy barriers that the mobile alkali ion must overcome in its jumps). The

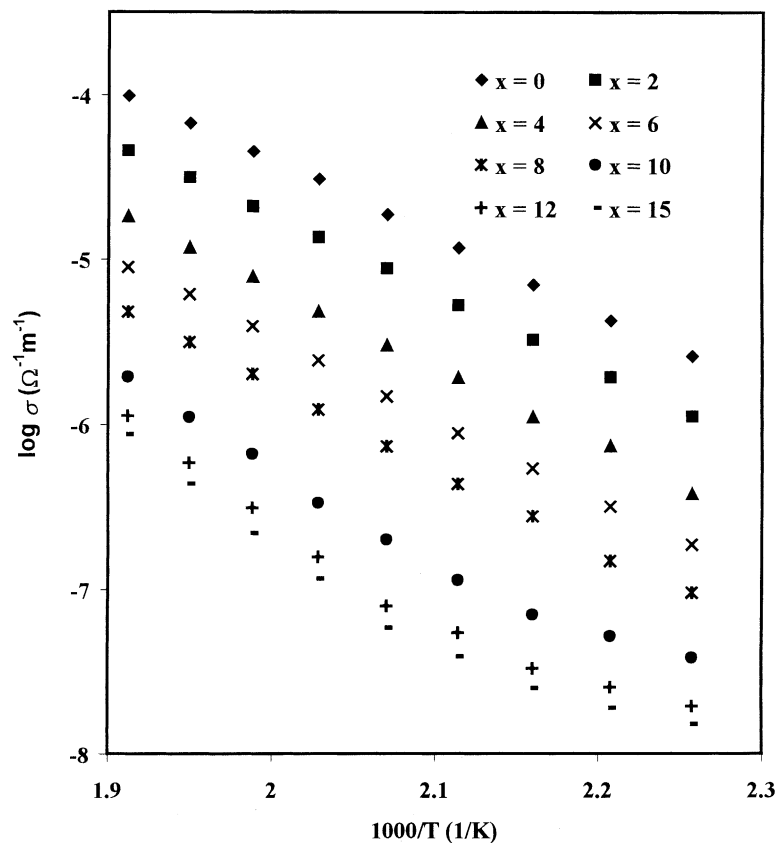
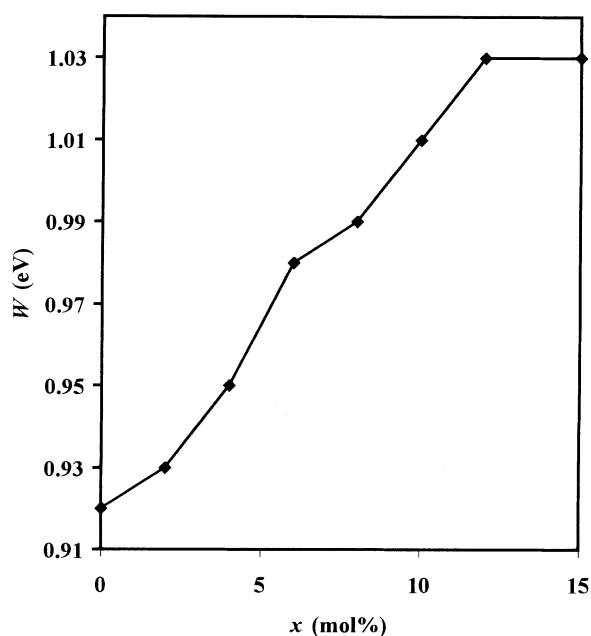


Fig. 3. Arrhenius plot of  $\sigma$  for  $x\text{Bi}_2\text{O}_3 \cdot (30-x)\text{K}_2\text{O} \cdot 70\text{B}_2\text{O}_3$  glasses.

Table 3

DC conductivity  $\sigma$ , activation energy  $W$  and  $\log \sigma_0$  of  $x\text{Bi}_2\text{O}_3 \cdot (30-x)\text{K}_2\text{O} \cdot 70\text{B}_2\text{O}_3$  glasses

Glass number	$x$ (mol%)	$\text{V}_2\text{O}_5$ (mol%)	$\sigma$ at 523 K ( $\Omega^{-1} \text{m}^{-1}$ )	$\sigma$ at 443 K ( $\Omega^{-1} \text{m}^{-1}$ )	$W$ (eV)	$\log \sigma_0$ ( $\Omega^{-1} \text{m}^{-1}$ )
1	0	2	$9.90 \times 10^{-5}$	$2.60 \times 10^{-6}$	0.92	4.84
2	2	2	$4.56 \times 10^{-5}$	$1.12 \times 10^{-6}$	0.93	4.62
3	4	2	$1.82 \times 10^{-5}$	$3.80 \times 10^{-7}$	0.95	4.45
4	6	2	$8.95 \times 10^{-6}$	$1.86 \times 10^{-7}$	0.98	4.39
5	8	2	$4.83 \times 10^{-6}$	$9.60 \times 10^{-8}$	0.99	4.26
6	10	2	$1.94 \times 10^{-6}$	$3.86 \times 10^{-8}$	1.01	3.88
7	12	2	$1.13 \times 10^{-6}$	$1.95 \times 10^{-8}$	1.03	3.82
8	15	2	$8.72 \times 10^{-7}$	$1.15 \times 10^{-8}$	1.03	3.64

Fig. 4. Variation of activation energy  $W$  with mol% of  $\text{Bi}_2\text{O}_3$  in  $x\text{Bi}_2\text{O}_3 \cdot (30-x)\text{K}_2\text{O} \cdot 70\text{B}_2\text{O}_3$  glasses.

pre-exponential factor,  $\sigma_0$ , contains several constants including the vibrational frequency of the mobile ion [23]. The values of  $W$ ,  $\log \sigma_0$  and  $\sigma$  at 443 and 523 K are shown in Table 3. The variation of activation energy with  $\text{Bi}_2\text{O}_3$  content is shown in Fig. 4. It is observed that the conductivity decreases with increase in  $\text{Bi}_2\text{O}_3:\text{K}_2\text{O}$  ratio (Fig. 3).

## 4. Discussion

### 4.1. EPR

Hecht and Johnston [6] studied extensively the EPR and optical spectra of  $\text{V}^{4+}$  ions in soda boric-oxide glasses and found that there are two ways, either by threefold symmetry or fourfold symmetry, to describe the crystal field of  $\text{V}^{4+}$  ions in glasses and concluded that the  $\text{V}^{4+}$  ions in their sodium-borate glasses must exist in octahedral coordination

with a tetragonal compression. The tetragonal compression was interpreted in terms of one of the V–O bonds being shorter than the other five, i.e., the ion in the glass was regarded as a vanadyl complex,  $\text{VO}^{2+}$ . An octahedral site with tetragonal compression would give  $g_{\parallel} < g_{\perp} < g_e$  and  $|A_{\parallel}| > |A_{\perp}|$  [6]. Hochstrasser [8] reached the same conclusion by comparing the measured spin Hamiltonian parameters with those previously reported for  $\text{V}^{4+}$  and  $\text{VO}^{2+}$  in other matrices. The values of the spin Hamiltonian parameters obtained in the present work satisfy this relationship and, therefore, it is confirmed that the  $\text{V}^{4+}$  ions in  $\text{Bi}_2\text{O}_3\text{:K}_2\text{O}\text{:B}_2\text{O}_3$  glasses exist as  $\text{VO}^{2+}$  ions in octahedral coordination with a tetragonal compression and belong to  $\text{C}_{4v}$  symmetry.

Tables 1 and 2 indicate that the values of  $g_{\parallel}$ ,  $A_{\parallel}$ ,  $P$ , and  $A'_{\parallel}$  decrease whereas the values of  $K$  and  $\Delta g_{\parallel}/\Delta g_{\perp}$  increase with increase in  $\text{Bi}_2\text{O}_3:\text{K}_2\text{O}$  ratio. The variation in the values of  $g_{\perp}$ ,  $A_{\perp}$ ,  $A'_{\perp}$  is within the experimental error. As suggested by Kivelson and Lee [16], the increase in the value of  $K$  with increase in  $\text{Bi}_2\text{O}_3:\text{K}_2\text{O}$  ratio is due [24–26] to an increase in the tetragonal nature of the  $\text{V}^{4+}\text{O}_6$  complex because of a strongly bonded oxygen at the  $\text{V}^{4+}$  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  $\text{K}_2\text{O}$  is replaced by  $\text{Bi}_2\text{O}_3$ . The decrease of the anisotropic contribution (i.e.,  $|A'_{\parallel}|$ ) of the  $3d_{xy}$  electron to the hyperfine splitting is brought about by increasing [20] 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  $\text{Bi}_2\text{O}_3:\text{K}_2\text{O}$  ratio.

The theoretical optical basicity 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, the optical basicity reflects the Lewis basicity of the oxide glasses. As the ability of the equatorial ligands to donate the electron (i.e., Lewis basicity) decreases,  $\sigma$ -bonding between  $\text{V}^{4+}$  and the ligands weakens [28]. This weakening, in turn, increases the positive charge on  $\text{V}^{4+}$  and strengthens the  $\pi$ -bondings between  $\text{V}^{4+}$  and vanadyl oxygen. This strengthening



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,  $A_{th}$ , of the host glass decreases when  $K_2O$  is replaced by  $Bi_2O_3$ . This decrease in  $A_{th}$  predicts that the tetragonal distortion should increase with increase in  $Bi_2O_3:K_2O$  ratio, keeping  $B_2O_3$  content constant. This prediction is in agreement with the EPR findings.

#### 4.2. Optical transmission

$(1 - \alpha^2)$  gives an indication of the effect of  $\sigma$ -bonding between vanadium and equatorial ligands, while  $(1 - \gamma^2)$  indicates the effect of  $\pi$ -bonding with the vanadyl oxygen. Table 2 shows that the value of  $\alpha^2$  increases with increase in  $Bi_2O_3:K_2O$  ratio, whereas the variation in  $\gamma^2$  is within experimental error. The decrease in the value of  $(1 - \alpha^2)$  indicates that the degree of covalency of the  $\sigma$ -bonding decreases with increase in  $Bi_2O_3:K_2O$  ratio in the present glass system. These observations are in agreement with the EPR results.

#### 4.3. DC conductivity

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

$$\sigma = Ne_z\mu \quad (13)$$

where  $N$  is the density of mobile ions of charge  $ez$  and of mobility  $\mu$ . The conductivity can vary with the variation in  $N$  and/or  $\mu$ . The mobility depends on the atomic structure that dictates the possible pathways available for migration [12]. In the present study,  $\sigma$  decreases and activation energy increases with increase in  $Bi_2O_3:K_2O$  ratio. The decrease in  $\sigma$  can be attributed to the decreasing number of mobile ionic carriers ( $K^+$  ions) and decrease in their mobility with increase in  $Bi_2O_3$  content. The conductivity is ionic in nature and there is no electronic contribution from  $Bi_2O_3$  because of electron hopping between  $Bi^{3+}$  and  $Bi^{5+}$  states in the present system [30]. The maximum conductivity is obtained for glass sample, which have maximum  $K_2O$  content. The increase in activation energy for conduction with increase in  $Bi_2O_3$  content indicates that the potential energy barriers to be overcome by the mobile alkali ion ( $K^+$ ) increases. In other words, we can say that the presence of  $Bi_2O_3$  shows ‘blocking effect’ on the migration of mobile ions rather than making any contribution in the form of electronic conductivity. Similar arguments were considered by other authors for the decrease in conductivity when in a binary glass, a third component was added [5,31,32].

## 5. Conclusions

In the investigated glass system,  $V^{4+}$  ions exist as  $VO^{2+}$  ions in octahedral coordination 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  $Bi_2O_3:K_2O$  ratio and increase in  $Bi_2O_3$  content results in an expansion of the  $3d_{xy}$  orbit of unpaired electron in the vanadyl ion. Theoretical optical basicity,  $A_{th}$ , predicts that the tetragonal distortion should increase with increase in  $Bi_2O_3:K_2O$  ratio, which is in agreement with EPR results. The values of the molecular orbital coefficients indicate that the degree of covalency decreases with increase in  $Bi_2O_3:K_2O$  ratio. The dc conductivity increases with increase in temperature. The order of conductivity is  $10^{-5} \Omega^{-1} m^{-1}$  at 523 K. The DC conductivity decreases and the activation energy increases with increase in  $Bi_2O_3:K_2O$  ratio because of decrease in number of mobile  $K^+$  ions and mobility. The dc conductivity is ionic in nature and there is no electronic contribution to it because of the addition of  $Bi_2O_3$  in potassium borate glasses.

## Acknowledgements

This work was supported by CSIR and UGC, New Delhi. One of the authors (AA) is also thankful to the DST, New Delhi, for financial support under DST-FIST scheme.

## References

- [1] A. Abragam, B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Clarendon Press, Oxford, 1970.
- [2] D.L. Griscom, *J. Non-Cryst. Solids* 40 (1980) 211.
- [3] J. Wong, C.A. Angell, *Glass Structure by Spectroscopy*, Dekker, New York, 1976.
- [4] N.J. Kreidl, *J. Non-Cryst. Solids* 123 (1990) 377.
- [5] S. Khasa, V.P. Seth, D. Prakash, P. Chand, *Radiat. Eff. Defects Solids* 140 (1997) 197.
- [6] H.G. Hecht, T.S. Johnston, *J. Chem. Phys.* 46 (1967) 23.
- [7] B. Bleaney, K.D. Bowers, M.H. Pryce, *Proc. R. Soc. London A* 228 (1955) 147.
- [8] G. Hochstrasser, *Phys. Chem. Glasses* 7 (1966) 178.
- [9] H. Toyuki, S. Akagi, *Phys. Chem. Glasses* 15 (1974) 1.
- [10] S. Khasa, V.P. Seth, A. Agarwal, R.M. Krishna, S.K. Gupta, P. Chand, *Mater. Chem. Phys.* 72 (2001) 366.
- [11] V.P. Seth, S. Gupta, A. Jindal, S.K. Gupta, *J. Non-Cryst. Solids* 162 (1993) 263.
- [12] M.D. Ingram, *Phys. Chem. Glasses* 28 (1987) 215.
- [13] B.V.R. Chowdari, Z. Rong, *Mater. Sci. Eng. B* 53 (1998) 241.
- [14] M. Dawy, A.H. Salama, *Mater. Chem. Phys.* 71 (2001) 137.
- [15] H.S. Liu, P.Y. Shih, T.S. Chin, *Phys. Chem. Glasses* 38 (1997) 123.
- [16] D. Kivelson, S. Lee, *J. Chem. Phys.* 41 (1964) 1896.
- [17] R. Muncaster, S. Parke, *J. Non-Cryst. Solids* 24 (1977) 399.
- [18] V. Heine, *Phys. Rev.* 107 (1957) 1002.
- [19] B.R. McGarvey, in: R.L. Carlin (Ed.), *Transition Metal Chemistry*, vol. 3, Dekker, New York, 1966, p. 115.
- [20] A.K. Bandopadhyay, *J. Mater. Sci.* 16 (1981) 189.
- [21] J.A. Duffy, M.D. Ingram, *J. Inorg. Nucl. Chem.* 37 (1975) 1203.
- [22] L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, New York, 1960, Chapter 13.
- [23] F. Branda, P. Pernice, A. Arome, C. Costantine, A. Buri, *Phys. Chem. Glasses* 31 (1990) 75.
- [24] H. Hosono, H. Kawazoe, T. Kanazawa, *J. Non-Cryst. Solids* 37 (1980) 427.
- [25] I. Ardelean, O. Cozar, Gh. Ilonca, *J. Non-Cryst. Solids* 68 (1984) 33.

- [26] V.P. Seth, A. Yadav, *Phys. Chem. Glasses* 28 (1986) 109.
- [27] A. Klonkowski, *Phys. Chem. Glasses* 26 (1985) 11.
- [28] H. Hosono, H. Kawazoe, T. Kanazawa, *J. Non-Cryst. Solids* 33 (1979) 125.
- [29] A.M. Glass, K. Nassau, *J. Appl. Phys.* 51 (1980) 3756.
- [30] K. Singh, *Solid State Ionics* 93 (1997) 147.
- [31] E.E. Khawaja, M.A. Khan, M.N. Khan, A.S.W. Li, J.S. Hwang, *J. Mater. Sci. Lett.* 3 (1984) 593.
- [32] M. Abid, M. Et-Tabirau, M. Taibi, *Mater. Sci. Eng. B* 97 (2003) 20.