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Electron paramagnetic resonance, optical transmission spectra and DC conductivity studies of vanadyl-doped alkali halide borate glasses

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Abstract

Electron paramagnetic resonance, optical transmission spectra and DC conductivity of the glasses $2xMX \cdot (0.30-x)M_2O \cdot 0.70B_2O_3$ (M = Na or K; X = Cl or Br) ($0.01 \leqslant x \leqslant 0.10$) containing $2.0\,mol\%$ of V_2O_5 have been studied. The spin-Hamiltonian parameters (SHP) of the VO^{2+} ions, the dipolar hyperfine parameter, P, the Fermi contact interaction parameter, K, and the molecular orbital coefficients (α^2 and γ^2) have been calculated. It is observed that in $KX \cdot K_2O \cdot B_2O_3$ (X = Cl or Br) glasses, the tetragonal nature of $V^{4+}O_6$ complex decreases with KBr for $x \geqslant 0.05$. An increase in the $2KX$:K_2O ratio ($x \geqslant 0.05$) also results in the contraction of 3dxy orbit of the unpaired electron in the vanadyl ion, whereas in case of $NaX \cdot Na_2O \cdot B_2O_3$ (X = Cl or Br) glasses, the SHP are independent of change in $2NaX$:M_2O ratio. It is observed that the SHP in these alkali halide borate glasses are independent of the theoretical optical basicity, Λ_{th}. It is also observed that the DC conductivity increases with increase in temperature. The order of conductivity is $10^{-6}\,\Omega^{-1}\,m^{-1}$ at low temperatures and $10^{-4}\,\Omega^{-1}\,m^{-1}$ at high temperatures. In $MCl \cdot M_2O \cdot B_2O_3$ (M = Na or K) glasses, the conductivity increases and the activation energy decreases with an increase in mol% of the NaCl or KCl content whereas, in $MBr \cdot M_2O \cdot B_2O_3$ (M = Na or K) glasses, the conductivity first increases and then decreases with mol% of the MBr content.
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1. Introduction

In earlier papers, electron paramagnetic resonance (EPR) studies of borate glasses containing transition metals (i.e. Co, Ni or Mo) were reported [1–5]. Study of the structure of alkali halide borate glasses is important because of their ionic conductivity and potential usage as solid electrolytes in various electrochemical devices with respect to solid-state batteries, fuel cells, chemical sensors, memory devices and

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smart windows. Glasses also have advantages over crystalline electrolytes such as isotropic conduction, the absence of grain boundaries and continuously varying composition. A particularly interesting class of fast-ion conductors is the metal halide-doped oxide glasses. In this class, much attention has been paid to lithium-ion-conducting glasses for developing high-energy density batteries [6–8]. In the present paper, a study of $MX \cdot M_2O \cdot B_2O_3$ (M = Na or K) (X = Cl or Br) glasses doped with V_2O_5 has been made in order to investigate the microstructure of the glasses. We have also carried out a systematic ion-conduction study of sodium and potassium halide-doped borate glasses.

2. Experimental

2.1. Glass preparation

Glasses with composition (i) $2xM\text{Cl} \cdot (0.3-x)$ $M_2O \cdot 0.7B_2O_3$ (M = Na or K) $(0.01 \leqslant x \leqslant 0.10)$ and (ii) $2xM\text{Br}(0.3-x)M_2O \cdot 0.7B_2O_3$ (M = Na or K) $(0.01 \leqslant x \leqslant 0.10)$ with $2.0\,\text{mol}\%$ of V_2O_5 were prepared by mixing Analar grade reagents NaCl, KCl, NaBr, KBr, Na_2CO_3, K_2CO_3, H_3BO_3 and V_2O_5 in a porcelain crucible. The mixture was melted in an electrical muffle furnace at 1273 K in air for about 30 min. A part of each sample was annealed at 473 K for 2 h.

2.2. EPR measurements

EPR spectra of annealed and unannealed glasses were recorded at room temperature using an EPR spectrometer (Varian E112) in the X-band ($\sim 9.14\,\text{GHz}$). A magnetic field modulation of 100 kHz with peak-to-peak amplitude of 0.1 mT was applied. Polycrystalline diphenyl picryl hydrazyl (DPPH) with $g = 2.0036$ was used as a field marker.

2.3. Optical transmission measurements

The optical transmission spectra of the vanadyl-doped alkali halide borate glasses were recorded at

room temperature using Perkin–Elmer UV/VIS spectrometer (Lambda 20) in the wavelength region 400–1000 nm.

2.4. DC conductivity measurements

To measure the DC conductivity, samples in the form of slices of nearly 1 mm thickness were chosen. Colloidal silver paint was used as an electrode material. Conductivity measurements were made by the standard technique, i.e. two-terminal method over a temperature range from about 300 to 523 K, first by increasing and then by decreasing the temperature. Measurements of DC conductivity were carried out using the device described by Khasa [2], which employs one sample at a time. A constant voltage of 10 V was applied across the sample and the circulating current was measured by using a Keithley 617 programmable electrometer/source. To minimize the polarization effects the current was passed only for a very short period (less than 30 s at a time). The polarity of the applied voltage across the sample was also reversed. Care was taken that the samples were not exposed to the moisture before performing the measurement.

3. Results

3.1. EPR

Figs. 1 and 2 show hyperfine lines in spectra of the VO^{2+} ion in unannealed $M\text{Cl} \cdot M_2O \cdot B_2O_3$ (M = Na or K) samples at 300 K. No change in the hyperfine coupling of VO^{2+} ions in the annealed samples reveals that there is no change in the EPR spectra on annealing. The spectra of these glasses show patterns very similar to those found in various alkali borate glasses containing vanadium [9,10] and have structures which are characteristic of a hyperfine interaction arising between an unpaired electron with the ^{51}V nucleus whose spin is 7/2 and which is present in 99.75% abundance [11]. These spectra were analyzed by assuming [1,12] that the vanadium is present as a vanadyl ion in a ligand field of C_{4V} symmetry. The spin
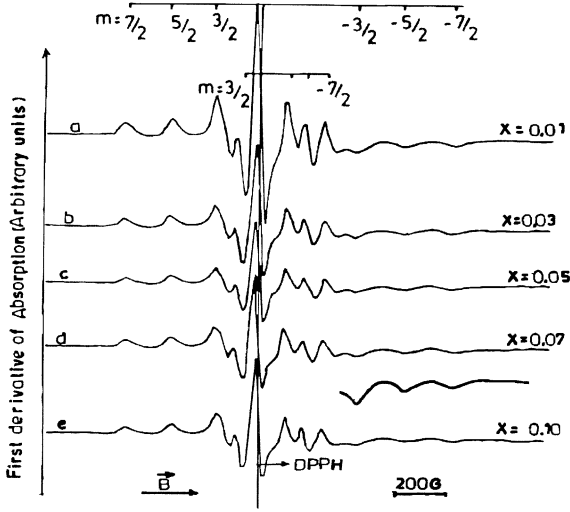
Fig. 1. EPR spectra of the VO^{2+} ion in unannealed $2x$NaBr·$(0.30-x)$Na$_2$O·0.70B$_2$O$_3$ $(0.01 \leqslant x \leqslant 0.10)$ glasses containing 2.0 mol% of V$_2$O$_5$ in the X-band at room temperature.
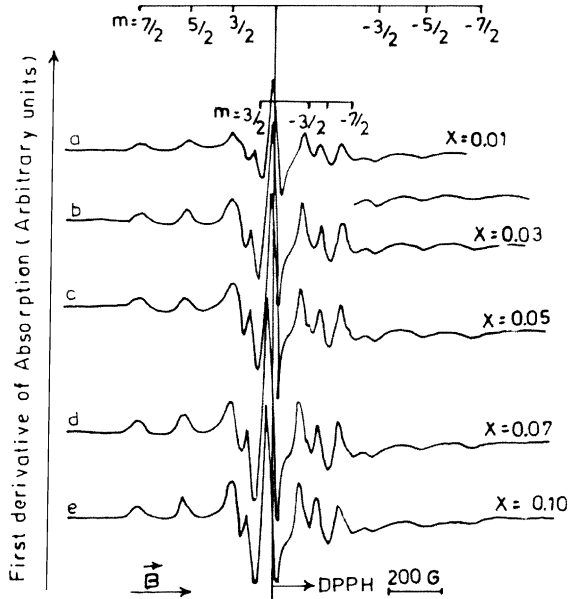
Fig. 2. EPR spectra of the VO^{2+} ion in unannealed $2x$KBr·$(0.30-x)$K$_2$O·0.70B$_2$O$_3$ $(0.01 \leqslant x \leqslant 0.10)$ glasses containing 2.0 mol% of V$_2$O$_5$ in the X-band at room temperature.

Hamiltonain used is of the form [9]

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

where the symbols have their usual meaning. Quadrupole and nuclear Zeeman interaction terms are ignored. The solutions [13] of the spin Hamiltonian (1) are given in Eqs. (2) and (3) for the parallel and perpendicular orientation, respectively:

$$B_{\|}(m) = B_{\|}(o) - mA_{\|} - \{\tfrac{63}{4} - m^2\}A_{\perp}^2/2B_{\|}(o), \tag{2}$$

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

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

$$B_{\|}(o) = h v/g_{\|}\beta \quad \text{and} \quad B_{\perp}(o) = h v/g_{\perp}\beta,$$

where h is Planck's constant, v is the frequency of the spectrometer and β is the Bohr magneton. The measurements for the $B_{\|}$ position were taken at the 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" [9]. Spin-Hamiltonian parameters (SHP) of VO^{2+} ion determined from the observed positions of spectral lines and using Eqs. (2) and (3) are given in Tables 1 and 2.

The uncertainty in the value of g is ± 0.001 and in the value of A, it is $\pm 1.0 \times 10^{-4}$ cm^{-1}. 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 by using the expressions developed by Kivelson and Lee [13]:

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

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

where $\Delta g_{\|} = g_{\|} - g_e$; $\Delta g_{\perp} = g_{\perp} - g_e$ and g_e $(= 2.0023)$ is the g factor of free electron. Both $A_{\|}$ and $A_{\perp}$ are found to be negative by the method proposed by Muncaster and Parke [11]. The term $-PK$ in Eqs. (4) and (5) is due to the s-character of the magnetic spin of vanadium. This s-character arises due to partial unpairing or polarization of the s electrons as a result of an interaction with the unpaired d electrons [14]. The effect of polarization on the hyperfine coupling was determined by

Table 1
Spin-Hamiltonian parameters[a] of VO^{2+} in unannealed $2xNaX \cdot (0.30-x)Na_2O \cdot 0.70B_2O_3$ [X=Cl (NC glasses) and Br (NB glasses)] glasses at room temperature

Glass no.	x	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}
NC1	0.01	2.0	1.9346	1.9685	168.4	61.6	5096
NC2	0.03	2.0	1.9346	1.9685	168.4	61.6	5022
NC3	0.05	2.0	1.9346	1.9685	168.4	61.6	4947
NC4	0.07	2.0	1.9352	1.9709	169.4	61.6	4873
NC5	0.10	2.0	1.9326	1.9697	169.2	62.1	4761
NB1	0.01	2.0	1.9358	1.9691	168.1	61.6	5098
NB2	0.03	2.0	1.9358	1.9691	168.1	61.6	5025
NB3	0.05	2.0	1.9355	1.9691	168.1	61.6	4953
NB4	0.07	2.0	1.9346	1.9691	168.4	61.6	4881
NB5	0.10	2.0	1.9346	1.9691	168.4	61.6	4773

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

Table 2
Spin-Hamiltonian parameters of VO^{2+} in unannealed $2xKX \cdot (0.30-x)K_2O \cdot 0.70B_2O_3$ [X=Cl (KC glasses) and Br (KB glasses)] glasses at room temperature

Glass no.	x	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}
KC1	0.01	2.0	1.9346	1.9685	167.5	61.6	5353
KC2	0.03	2.0	1.9346	1.9685	167.5	61.6	5261
KC3	0.05	2.0	1.9346	1.9685	168.4	61.6	5169
KC4	0.07	2.0	1.9369	1.9708	169.5	61.6	5077
KC5	0.10	2.0	1.9329	1.9703	169.2	62.3	4938
KB1	0.01	2.0	1.9346	1.9708	167.1	61.6	5355
KB2	0.03	2.0	1.9346	1.9708	167.1	61.6	5265
KB3	0.05	2.0	1.9352	1.9703	169.4	61.5	5175
KB4	0.07	2.0	1.9352	1.9715	168.9	62.6	5085
KB5	0.10	2.0	1.9326	1.9715	169.2	62.6	4951

Heine [14] and is included as $-PK$ in the expression for hyperfine coupling. For transition metal ions, K is found to be positive [15]. From the molecular orbital theory, it can also be shown [16] that the components $A_\parallel$ and $A_\perp$ consist of the contributions $A'_\parallel$ and $A'_\perp$ of the electron to the HFS and the PK term which arises due to the anomalous contribution of the s electrons. Eqs. (4) and (5) can be rewritten in the following form:

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

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

Calculated values of $A'_\parallel$ and $A'_\perp$ are given in Tables 3 and 4.

The theoretical optical basicity Λ_{th} has also been calculated [17] by using the expression

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

where Z_i is the oxidation number of the cation i, r_i is the ratio of the 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

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

where x_i is the Pauling electronegativity [18] of the cation. The calculated value of Λ_{th} of glasses is given in Tables 1 and 2.

Table 3
P, K, $|A'_\parallel|$, $|A'_\perp|$, $\Delta g_\parallel/\Delta g_\perp$, α^2 and γ^2 of VO^{2+} in unannealed $2x\text{Na}X \cdot (0.3-x)\text{Na}_2\text{O} \cdot 0.70\text{B}_2\text{O}_3$ [X = Cl (NC glasses) and Br (NB glasses)] glasses at room temperature

Glass no.	P $(10^{-4}\,\text{cm}^{-1})$	K	$|A'_\parallel|$ $(10^{-4}\,\text{cm}^{-1})$	$|A'_\perp|$ $(10^{-4}\,\text{cm}^{-1})$	$\Delta g_\parallel/\Delta g_\perp$	α^2	γ^2
NC1	117.1	0.785	76.5	30.3	2.0027	0.6051	0.8539
NC2	117.1	0.785	76.5	30.3	2.0027	0.6051	0.8539
NC3	117.1	0.785	76.5	30.3	2.0027	0.6051	0.8539
NC4	118.0	0.783	76.9	30.8	2.1362	0.5998	0.7933
NC5	117.0	0.790	76.6	30.4	2.1374	0.623	0.8236
NB1	116.8	0.787	76.2	30.3	2.0040	0.6063	0.8593
NB2	116.8	0.787	76.2	30.3	2.0040	0.6063	0.8593
NB3	116.7	0.787	76.2	30.3	2.0126	0.609	0.8593
NB4	117.0	0.786	76.5	30.4	2.0386	0.6172	0.8593
NB5	117.0	0.786	76.5	30.4	2.0386	0.6172	0.8593

Table 4
P, K, $|A'_\parallel|$, $|A'_\perp|$, $\Delta g_\parallel/\Delta g_\perp$, α^2 and γ^2 of VO^{2+} in unannealed $2x\text{K}X \cdot (0.3-x)\text{K}_2\text{O} \cdot 0.70\text{B}_2\text{O}_3$ [X = Cl (KC glasses) and Br (KB glasses)] glasses at room temperature

Glass no.	P $(10^{-4}\,\text{cm}^{-1})$	K	$|A'_\parallel|$ $(10^{-4}\,\text{cm}^{-1})$	$|A'_\perp|$ $(10^{-4}\,\text{cm}^{-1})$	$\Delta g_\parallel/\Delta g_\perp$	α^2	γ^2
KC1	116.1	0.789	75.9	30.1	2.0027	0.604	0.8571
KC2	116.1	0.789	75.9	30.1	2.0027	0.604	0.8571
KC3	117.1	0.785	76.5	30.3	2.0027	0.604	0.8571
KC4	118.4	0.782	77.0	30.9	2.0813	0.5835	0.7987
KC5	116.8	0.794	76.4	30.4	2.1682	0.6192	0.8114
KB1	115.4	0.795	75.3	30.1	2.1545	0.6172	0.8131
KB2	115.4	0.795	75.3	30.1	2.1545	0.6172	0.8131
KB3	117.1	0.795	76.3	30.5	2.0964	0.6117	0.826
KB4	116.5	0.799	75.9	30.4	2.1775	0.6117	0.7951
KB5	116.5	0.799	76.1	30.4	2.2613	0.6355	0.7951

3.2. Optical transmission

For all the glasses only two transmission bands are observed. Fig. 3 shows the typical optical transmission spectra of the vanadyl ion in $\text{KCl} \cdot \text{K}_2\text{O} \cdot \text{B}_2\text{O}_3$ glasses. For $\text{KCl} \cdot \text{K}_2\text{O} \cdot \text{B}_2\text{O}_3$ ($\text{KBr} \cdot \text{K}_2\text{O} \cdot \text{B}_2\text{O}_3$) glasses, these bands are at 791 nm (777 nm) and at 562 nm (550 nm). Similarly, for $\text{NaCl} \cdot \text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$ ($\text{NaBr} \cdot \text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$) glasses these two bands are at 794 nm (775 nm) and at 561 nm (550 nm). These two bands are typical for VO^{2+} and can be assigned to $b_2 \rightarrow e_\Pi^*$ and $b_2 \rightarrow b_1^*$ transitions. The values of $g_\parallel$ and $g_\perp$ are related to bonding parameters by the following equations [16]:

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

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

where E_1 and E_2 are the energies of transition ($b_2 \rightarrow e_\Pi^*$) 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 1 for many glasses containing VO^{2+} ions [17]. λ is the spin orbit coupling constant and is equal to 249 cm^{-1} [11]. $(1 - \alpha^2)$ 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 3 and 4.

3.3. DC conductivity

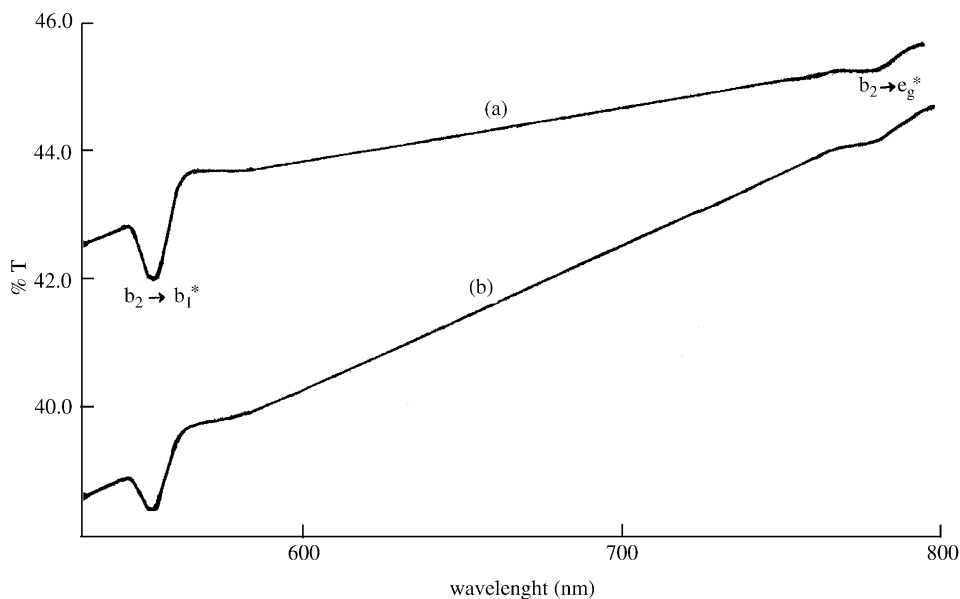Figs. 4 and 5 show the temperature dependence of the DC conductivity of the

Fig. 3. Optical transmission spectra of $2x$KCl·$(0.30-x)$K$_2$O·0.70B$_2$O$_3$ glasses at room temperature: (a) $x = 0.03$ and (b) $x = 0.10$.
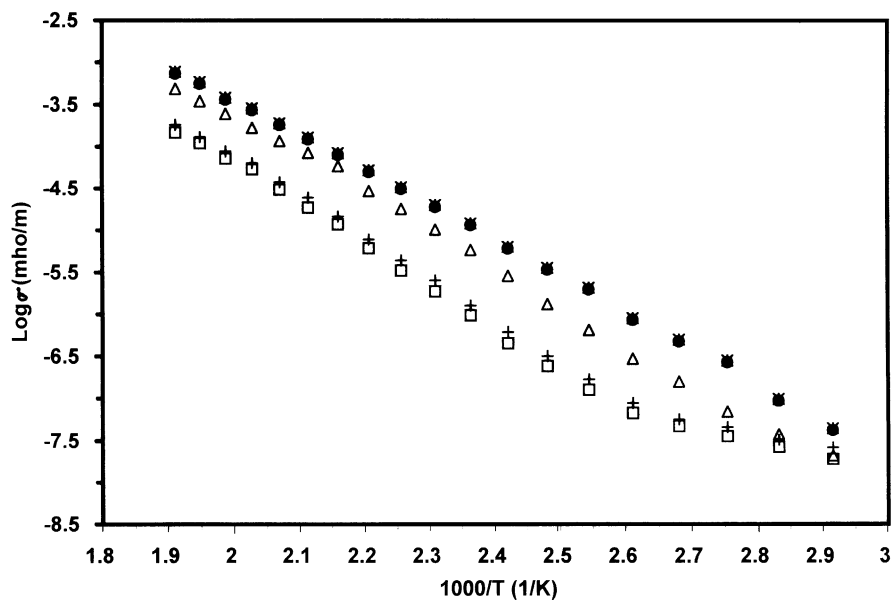

Fig. 4. Variation of $\log \sigma$ as a function of $1/T$ for glasses KC1 ($\square$), KC2 ($+$), KC3 ($\triangle$), and KC4 ($\bullet$), KC5 ($*$).

$2x$KX·$(0.3-x)$K$_2$O·0.7B$_2$O$_3$ (X= Cl or Br) (0.01 $\leqslant x \leqslant 0.10$) ternary glasses. The linear relationship between the logarithm of the DC conductivity

($\log \sigma$, σ is measured in $\Omega^{-1}\,m^{-1}$) and inverse of temperature ($1/T$, T measured in K) with a negative slope indicates that the ionic
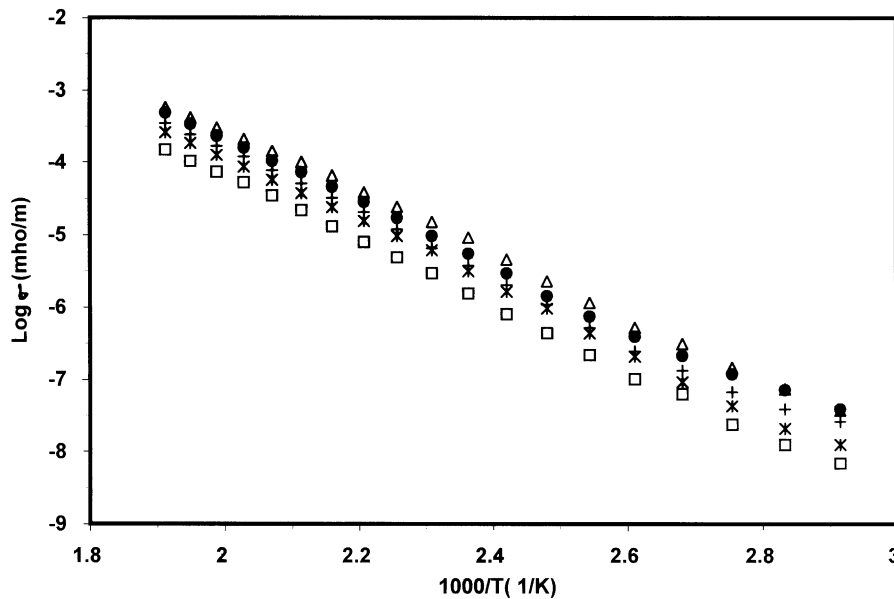
Fig. 5. Variation of $\log \sigma$ as a function of $1/T$ for glasses KB1 ($\square$), KB2 ($+$), KB3 ($\triangle$), KB4 ($\bullet$), and KB5 (*).

Table 5
DC conductivity, σ, activation energy, W, and pre-exponential term, $\log \sigma_0$, of the $2xM\mathrm{Cl} \cdot (0.30-x)M_2\mathrm{O} \cdot 0.70\mathrm{B}_2\mathrm{O}_3$ ($M = $ Na and K) glasses

Glass no.	x	V_2O_5 (mol%)	$\sigma_{\mathrm{at\ 513\ K}}$ $(\Omega^{-1}\mathrm{m}^{-1})$	$\sigma_{\mathrm{at\ 423\ K}}$ $(\Omega^{-1}\mathrm{m}^{-1})$	$\log \sigma_0$	W (eV)
NC1	0.01	2.0	02.5×10^{-4}	03.1×10^{-6}	5.67	0.94
NC2	0.03	2.0	03.7×10^{-4}	05.3×10^{-6}	5.53	0.90
NC3	0.05	2.0	06.5×10^{-4}	13.2×10^{-6}	5.01	0.83
NC4	0.07	2.0	09.9×10^{-4}	21.1×10^{-6}	5.24	0.83
NC5	0.10	2.0	13.5×10^{-4}	28.8×10^{-6}	5.37	0.83
KC1	0.01	2.0	01.1×10^{-4}	01.0×10^{-6}	5.82	0.99
KC2	0.03	2.0	01.3×10^{-4}	01.3×10^{-6}	5.73	0.97
KC3	0.05	2.0	03.5×10^{-4}	05.8×10^{-6}	5.26	0.88
KC4	0.07	2.0	05.6×10^{-4}	11.5×10^{-6}	4.75	0.81
KC5	0.10	2.0	05.9×10^{-4}	12.1×10^{-6}	4.77	0.81

conductivity follows the following relation developed by Rasch–Hinrichsen:

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

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

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

The calculated values of W and $\log \sigma_0$ are presented in Tables 5 and 6. The values of the conductivity at 513 and at 423 K are also included in Tables 5 and 6. From these tables and Figs. 4 and 5, it is observed that the DC conductivity increases with increase in temperature and the DC conductivity decreases when Na_2O is replaced by

Table 6
DC conductivity, σ, activation energy, W, and pre-exponential term, $\log \sigma_0$, of the $2xM\mathrm{Br} \cdot (0.30-x)M_2\mathrm{O} \cdot 0.70\mathrm{B}_2\mathrm{O}_3$ ($M =$ Na and K) glasses

Glass no.	x	$\mathrm{V}_2\mathrm{O}_5$ (mol%)	$\sigma_{\text{at 513 K}}$ ($\Omega^{-1}\mathrm{m}^{-1}$)	$\sigma_{\text{at 423 K}}$ ($\Omega^{-1}\mathrm{m}^{-1}$)	$\log \sigma_0$	W (eV)
NB1	0.01	2.0	04.30×10^{-4}	07.90×10^{-6}	5.01	0.85
NB2	0.03	2.0	06.20×10^{-4}	08.60×10^{-6}	5.61	0.89
NB3	0.05	2.0	07.81×10^{-4}	16.59×10^{-6}	4.96	0.81
NB4	0.07	2.0	08.00×10^{-4}	08.00×10^{-6}	5.49	0.89
NB5	0.10	2.0	03.80×10^{-4}	05.80×10^{-6}	5.23	0.89
KB1	0.01	2.0	01.00×10^{-4}	01.50×10^{-6}	4.78	0.89
KB2	0.03	2.0	02.40×10^{-4}	03.70×10^{-6}	5.03	0.87
KB3	0.05	2.0	04.20×10^{-4}	09.20×10^{-6}	4.78	0.83
KB4	0.07	2.0	03.40×10^{-4}	05.50×10^{-6}	5.13	0.87
KB5	0.10	2.0	01.80×10^{-4}	03.10×10^{-6}	4.86	0.87

$\mathrm{K}_2\mathrm{O}$ keeping $\mathrm{B}_2\mathrm{O}_3$ and MX constant. It is also observed that the DC conductivity increases when $\mathrm{Na}_2\mathrm{O}$ ($\mathrm{K}_2\mathrm{O}$) is replaced by NaCl (KCl) in $\mathrm{NaCl} \cdot \mathrm{Na}_2\mathrm{O} \cdot \mathrm{B}_2\mathrm{O}_3$ ($\mathrm{KCl} \cdot \mathrm{K}_2\mathrm{O} \cdot \mathrm{B}_2\mathrm{O}_3$) samples and activation energy decreases up to $x = 0.05$ ($x = 0.07$) in $\mathrm{NaCl} \cdot \mathrm{Na}_2\mathrm{O} \cdot \mathrm{B}_2\mathrm{O}_3$ ($\mathrm{KCl} \cdot \mathrm{K}_2\mathrm{O} \cdot \mathrm{B}_2\mathrm{O}_3$) samples, and on further increase in x, the activation energy becomes constant; whereas the DC conductivity first increases and then decreases continuously when $M_2\mathrm{O}$ is gradually replaced by $M\mathrm{Br}$ and the activation energy first decreases and then increases with increase in $2M\mathrm{Br}:M_2\mathrm{O}$ ratio. The DC conductivity is of the order of $10^{-4}\,\Omega^{-1}\,\mathrm{m}^{-1}$ at high temperatures (513 K) and is of the order of $10^{-6}\,\Omega^{-1}\,\mathrm{m}^{-1}$ at low temperatures (343 K), even at very low alkali chloride content (i.e. $x \leqslant 0.10$). This value is comparable to the values for borate and phosphate glasses containing alkali chloride and alkali oxide [19–22]. Since the vanadium ions in these glasses may exist in more than one-valence state, e.g. V^{4+} and V^{5+}, conduction could also take place by the transfer of electrons from low to high valence states. The decrease of 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 role in the total conductivity. So the alkali halide borate glasses under study can be considered as fast alkali-ion-conducting glasses.

4. Discussion

4.1. EPR

Tables 2 and 4 show that $g_\parallel$, $g_\perp$, $A_\parallel$, $A_\perp$, P, $A'_\parallel$, $A'_\perp$ and $\Delta g_\parallel / \Delta g_\perp$ increase and that K decreases slightly in $2\mathrm{KCl} \cdot \mathrm{K}_2\mathrm{O} \cdot \mathrm{B}_2\mathrm{O}_3$ samples for $x = 0.07$. The minimum value of K at $x = 0.07$ suggests [23–26] a decrease in the tetragonal nature of the $\mathrm{V}^{4+}\mathrm{O}_6$ complex at this composition of the system because of a strongly bonded oxygen atom to the V^{4+} ion at the site opposite to the vanadyl oxygen atom. However, the increase in $\Delta g_\parallel / \Delta g_\perp$ with KCl content in the unannealed samples suggests that the tetragonal nature of the $\mathrm{V}^{4+}\mathrm{O}_6$ complex is enhanced with increasing concentration of KCl. The increase of the anisotropic contribution of the $3d_{xy}$ electron to the hyperfine splitting at $x = 0.07$ is brought about by the decreasing screening [16] of the $3d_{xy}$ orbital from its nucleus through overlap of the electron orbits of the surrounding oxygen ligands. This produces a contraction of the $3d_{xy}$ orbital, resulting in an increased interaction between the electron and the vanadium nucleus. The increase in the value of P also supports the argument that $3d_{xy}$ orbit contracts in the system at $x = 0.07$.

The values for $g_\parallel$, $g_\perp$, $A_\parallel$, $A_\perp$, P, K, $A'_\parallel$, $A'_\perp$ and $\Delta g_\parallel / \Delta g_\perp$ are shown in Tables 2 and 4 for $2x\mathrm{KBr} \cdot (0.30-x)\mathrm{K}_2\mathrm{O} \cdot 0.70\mathrm{B}_2\mathrm{O}_3$ ($0.01 \leqslant x \leqslant 0.10$) samples. It is observed that the $\Delta g_\parallel / \Delta g_\perp$ shows a minimum at $x = 0.05$ indicating that the octahedral symmetry at the $\mathrm{V}^4\mathrm{O}_6$ complex is

maximum for this composition. The increase of the anisotropic contribution (i.e., $A'_{\parallel}$ and $A'_{\perp}$, although the increase in $A'_{\perp}$ is within experimental error) for $x = 0.05$ of the 3dxy electron to the hyperfine splitting is brought about by the decreased screening of the 3dxy orbital from its nucleus through overlap of the electron orbits of the surrounding oxygen ligands. This decrease produces a contraction of the 3dxy orbital, resulting in an increased interaction between this 3dxy electron with the vanadium nucleus. An increase in the value of P also supports the argument that 3dxy orbit contracts in the glasses $KBr \cdot K_2O \cdot B_2O_3$ for $x = 0.05$.

Table 1 shows that the variation in $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$ and $A_{\perp}$ is within experimental error with an increase in mol% of NaX in $NaX \cdot Na_2O \cdot B_2O_3$ ($X = $ Cl or Br) samples. The SHP are independent of the concentration of NaX.

The theoretical optical basicity serves in first approximation as a measure [26] for the ability of oxygen to donate a negative charge in the glass. 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, σ bondings between V^{4+} and the ligands are reduced [27]. This reduction, in turn, increases the positive charge on V^{4+} and increases the π bonding between the V^{4+} and the vanadyl oxygen. This increase of the π bonding decreases the bond length of V^{4+}–(vanadyl oxygen). Consequently, the tetragonal nature of the $V^{4+}O_6$ complex is enhanced.

Calculated values of the theoretical optical basicity Λ_{th} are included in Tables 1 and 2. The value of Λ_{th} decreases with increase in the mol% of MX ($M = $ Na or K, $X = $ Cl or Br). This behavior suggests that the tetragonal nature of the $V^{4+}O_6$ complex should increase with increasing MX concentration in the system. This indicates that the value of Λ_{th} is independent of the SHP in $MX \cdot M_2O \cdot B_2O_3$ samples.

4.2. Optical transmission

$(1 - \alpha^2)$ gives an indication of the effect of the σ bonding between the vanadium atom and the equatorial ligands, while $(1 - \gamma^2)$ indicates the effect of the π bonding with the vanadyl oxygen. From Tables 3 and 4 it is observed that α^2 and γ^2 show a minimum at $x = 0.07$ in $MCl \cdot M_2O \cdot B_2O_3$ ($M = $ Na or K) glasses which indicates that the covalency of the vanadium oxygen bonds is maximum at this composition. For $NaBr \cdot Na_2O \cdot B_2O_3$ glasses, α^2 increases with increasing 2NaBr: Na$_2$O ratio but this increase is within experimental error because the decrease in $g_{\parallel}$ is within experimental error whereas γ^2 is constant in these glasses. Thus, for these glasses there is no change in the covalency rates. For $KBr \cdot K_2O \cdot B_2O_3$ glasses, α^2 has a minimum at $x = 0.05$ whereas γ^2 decreases with increasing 2KBr:K$_2$O ratio, except at $x = 0.05$, indicating that the covalency changes at this composition.

4.3. DC conductivity

4.3.1. DC conductivity of $MCl \cdot M_2O \cdot B_2O_3$ ($M = Na$ or K) system

Figs. 4, 6 and 7 and Table 5 suggest that for low concentrations of alkali chlorides, the DC conductivity and the activation energy are strongly dependent on the $2MCl:M_2O$ ratio. This dependence of the activation energy and the conductivity may be due to the fact the M–Cl bonds are weaker than the M–O bonds, so the number of mobile alkali ions increases with increasing MCl content and this mobility of the alkali ions is in accordance with the diffusion-path model proposed by Minami [28]. Furthermore, the glass structure becomes more open due to the formation of non-bridging oxygens by adding alkali chloride, which may create a diffusion path, and, hence, as a result of this, the conductivity increases and activation energy decreases upon addition of alkali chloride.

4.3.2. DC conductivity of $MBr \cdot M_2O \cdot B_2O_3$ ($M = Na$ or K) system

From Fig. 5 and Table 6 it is observed that the DC conductivity measured in alkali bromide borate glass increases with a small increase in the concentration of MBr in the range $0.01 \leqslant x \leqslant 0.05$ but decreases on further addition of MBr (up to 10.0 mol%). This shows that the addition of MBr in low concentrations modifies the conduction

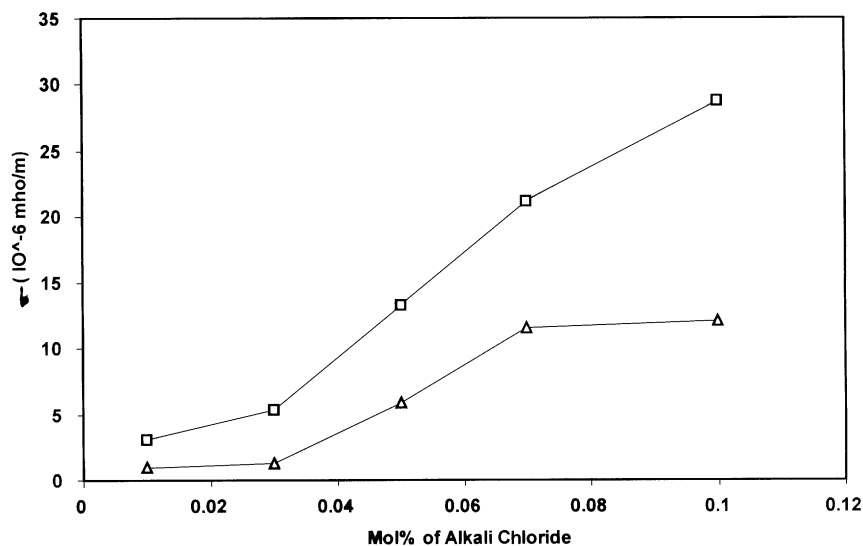Fig. 6. Composition dependence of the DC conductivity in $2xM\mathrm{Cl}\cdot(0.30-x)M_2\mathrm{O}\cdot0.70\mathrm{B}_2\mathrm{O}_3$ glasses at 423 K (($\square$) Na and ($\triangle$) K).
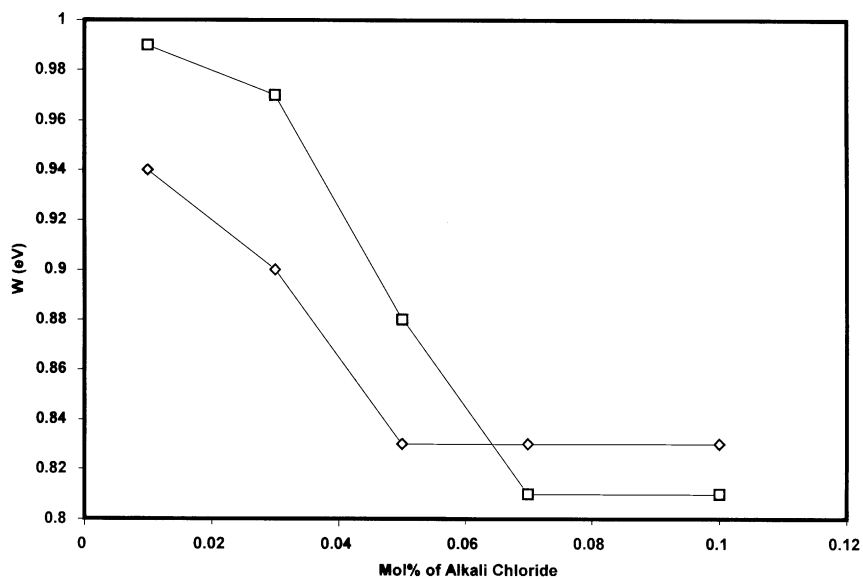
Fig. 7. Composition dependence of the activation energy in $2xM\mathrm{Cl}\cdot(0.30-x)M_2\mathrm{O}\cdot0.70\mathrm{B}_2\mathrm{O}_3$ glasses at 423 K (($\square$) Na and ($\triangle$) K).

property in a systematic manner. However, at higher concentrations ($x > 0.05$) the decrease in the conductivity is due to the formation of clusters. Because of the high concentration of MBr, the dispersion of bromine is no longer uniform but it rather forms clusters which tend to aggregate as further bromine is added and becomes therefore

less effective in acting as a generally dispersed oxidizing agent. The result of this behavior in the present system is that for $x > 0.05$ the activation energy increases. A similar argument was considered by Hogarth [29] for the change in the conductivity of copper phosphate glasses when copper chloride is added.

5. Conclusions

1. The site symmetry around the V^{4+} ion in $MCl \cdot M_2O \cdot B_2O_3$ (M = Na or K) and in $MBr \cdot M_2O \cdot B_2O_3$ (M = Na or K) glasses is octahedral with tetragonal distortion (C_{4V} symmetry).

2. In $NaX \cdot Na_2O \cdot B_2O_3$ (X = Cl or Br) glasses, the tetragonal distortion remains unaffected with the increase in mol% of NaX. The tetragonal distortion of the $V^{4+}O_6$ complex is enhanced at $x \geqslant 0.07$ ($x \geqslant 0.05$) in $KCl \cdot K_2O \cdot B_2O_3$ ($KBr \cdot K_2O \cdot B_2O_3$) glasses.

3. In $KCl \cdot K_2O \cdot B_2O_3$ ($KBr \cdot K_2O \cdot B_2O_3$) samples, the 3dxy orbital of the vanadium ion contracts for $x = 0.07$ ($x = 0.05$).

4. In $NaCl \cdot Na_2O \cdot B_2O_3$ ($NaBr \cdot Na_2O \cdot B_2O_3$) samples, the SHP are independent of the concentration of NaCl and NaBr.

5. The SHP are independent of the theoretical optical basicity in $MX \cdot M_2O \cdot B_2O_3$ (M = Na or K, X = Cl or Br) glasses.

6. α^2 and γ^2 show a minimum at $x = 0.07$ in $MCl \cdot M_2O \cdot B_2O_3$ (M = Na or K) glasses which indicates that the covalency of the vanadium oxygen bonds is maximum at this composition.

7. For $NaBr \cdot Na_2O \cdot B_2O_3$ glasses there is no change in the covalency rates.

8. For $KBr \cdot K_2O \cdot B_2O_3$ glasses the covalency rates change at composition $x = 0.05$.

9. The DC conductivity decreases when Na_2O is replaced by K_2O keeping B_2O_3 and MX constant.

10. The order of magnitude of the conductivity in $MCl \cdot M_2O \cdot B_2O_3$ ($MBr \cdot M_2O \cdot B_2O_3$) ($M$ = Na or K) samples is $10^{-6}\,\Omega^{-1}\,m^{-1}$ at low temperatures and $10^{-4}\,\Omega^{-1}\,m^{-1}$ at high temperatures, so that such glasses can be considered as fast alkali-ion-conducting glasses.

11. The activation energy decreases only up to $x = 0.03$ with increase in chloride ions in alkali-chloro-borate glass. For $x \geqslant 0.05$ ($x \geqslant 0.07$) the activation energy is constant and it does not depend on the value of x in $NaCl \cdot Na_2O \cdot B_2O_3$ ($KCl \cdot K_2O \cdot B_2O_3$) samples.

12. The DC conductivity of alkali bromide borate glass increases with small increase of MBr in the range $0.01 \leqslant x \leqslant 0.05$, but it decreases on further addition of MBr.

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