Electron Spin Resonance of V^{4+} Ions in K_2O-B_2O_3-V_2O_5 Glasses

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Abstract

In the present work the ESR study of potassium borovanadate (K_2O-B_2O_3-V_2O_5) glasses is reported at room temperature and liquid nitrogen temperature. The spectra at liquid nitrogen temperature is similar to at room temperature except the indusial hyperfine lines are sharper and more intense which might be ascribed to a spin-lattice relaxation effect. The ESR parameters were calculated at room temperature and a show that in-plane π bonding is somewhat covalent and covalency is nearly independent of concentration of K_2O. The octahedral site with a tetragonal compression gives g value in the order $g_{ll} < g_{\perp} < g_e (=2.0023)$. It is observed that the V^{4+} ions in the present sample exist as VO^{2+} ions in octahedral coordination with a tetragonal compression and belong to C_{4v} symmetry.

Keywords: E.S.R., Borate glasses, Spin-Hmiltonian

Introduction

Election spin resonance (ESR) of V^{4+} ions in various borate, sulphate and oxide glasses have been studied in the past [1-12]. The ESR of vanadium doped glasses [8,12] indicated that the V^{4+} ions in these glasses were present as a vanadyl-type structure in a ligand field with a fourfold symmetry (C_{4v} symmetry). The coordination of the VO^{2+} ions is found to vary with the concentration of alkali oxide. In these investigations [1-12], however, the concentration of vanadium was very low so that it could serve as a spectroscopic probe or impurity in the glasses. Not much work has been reported on vanadium rich glasses. In the present work the ESR study of potassium borovanadate (K_2O-B_2O_3-V_2O_5) glasses, in which V_2O_5 is major constituent of glass is therefore, called for. In addition, the results are compared with those of vanadium doped in alkali borate glasses.

Experimental

The K_2O-B_2O_3-V_2O_5 (KBV) glasses were prepared by mixing Analar grade reagents of K_2CO_3, V_2O_5 and H_3BO_3, in appropriate proportions (here the molecular ratio V_2O_5 / B_2O_3 =1). Each batch was first sintered for about three hours at 500±50°C in order to convert carbonate in oxide and boric acid into B_2O_3, and then melted in porcelain crucibles in an electric muffle furnace. The melt was poured on to a carbon plate and was pressed immediately with another plate. The compositions of the samples are shown in Table 1. The ESR studies were performed on a JEOL JES FE-3X homodyne spectrometer operating at 9.45 GHz equipped with a TE_{011}-cylindrical cavity and 100 KHz field modulation. The ESR

spectra at liquid nitrogen temperature were also recorded using a JES-UCD-2X insertion type dewar vessal.

Results and discussions

Figure 1 shows the ESR spectra of all the samples at room temperature (⁓290K). The spectra of the samples are found to be similar to those of various vandiun doped borate and oxide glasses [8, 12]. The ESR spectra at liquid nitrogen temperature (⁓77K) are very similar to those at room temperature except that the individual hyperfine lines are sharper and more intense which might be ascribed to a spin-lattice relaxation effect.

Figure 1. ESR Spectra of V^{4+} Ions in K_2O-B_2O_3-V_2O_5 Glasses
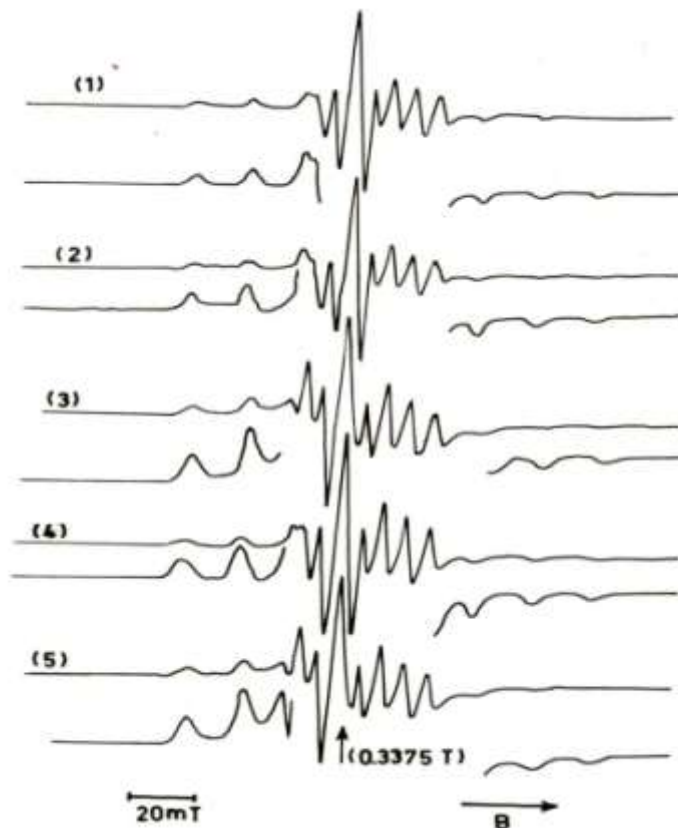
The spectra show a structure which is characteristic of hyperfine interaction of a single unpaired electron with a ^{51}V (99.8% abundant, I=7/2) nucleus.

The spectra were analysed using an axial spin-Hamiltonian of the form

$$H = \beta g_{\parallel}B_Z S_Z + \beta g_{\perp}(B_X S_X + B_y S_y) + A_{\parallel} S_Z I_Z + A_{\perp} (S_X I_X + S_y I_y) \quad \dots(1)$$

where the symbols have their usual meanings. It is to be noted that quadrupole and nuclear Zeeman interaction terms have been ignored [7,13].

The solutions of the spin-Hamiltonian for the parallel and perpendicular hyperfine lines respectively are

$$B_{\parallel}(m) = B_{\parallel}(o) - mA_{\parallel} - [I(I+1) - m^2] A^2_{\perp} / 2B_{\parallel}(o) \quad \dots\dots(2)$$

$$B_\perp (m) = B_\perp (o) - mA_\perp - [I(I+1) - m^2] (A^2_\parallel + A^2_\perp) / 4B_\perp (o) \qquad \ldots\ldots(3)$$

Where $\quad B_\parallel (o) = h\nu / g_\parallel\beta, \qquad B_\perp (o) = h\nu / g_\perp\beta,$

and m is the magnetic quantum number of the vanadium nucleus. Measurements for the B_{II}, positions were done which correspond to maximum in the first derivative curve of the parallel hyperfine components for a given value, whereas the $B_\perp$ position is enclosed between the first derivative perpendicular peak and its "zero"[9]. The spin Hamiltonian parameters were determined using eqs. (2) and (3) and are given in Table 1. It is observed from Table 1 that A_{II}, and $A_\perp$ increase slightly as the concentration of K_2O increases, while the values of g_{II} and $g_\perp$ show no significant changes. The molecular orbital analysis was made using the relations given by Kivelson and Lee of the form [11]

$$A_\parallel = P[-\beta_2^{*2} (4/7+ k) + (g_\parallel - 2.0023) + 3/7 (g_\perp - 2.0023) + D_\parallel + 3/7 D_\perp] \quad\ldots..(4)$$

$$A_\perp = P [\beta_2^{*2} (2/7- k) + 11/14 (g_\perp - 2.0023) + 11/14 D_\perp] \qquad\qquad\ldots..(5)$$

where β_2^* is the coefficient of ion wave function corresponding to antibonding orbitals, $P=2\Upsilon\beta\beta_N< r^{-3} >$ or P is proportional to the average value of $1/r^3$ for the free ion (r-is the distance of unpaired electron to the ^{51}V nucleus) [11] and k is the contribution to the hyperfine coupling due to the isotropic Fermi contact interaction [9],

$$k \propto< \phi^*_{\beta 2}| \Sigma \delta(r_k) S_k| \phi^*_{\beta 2}> \qquad\qquad\ldots.(6)$$

Here S_k is the spin operator of the kth electron, δ is the function operator evaluated in the ground state and r_k is the displacement of kth electron from nucleus.

The wave functions of relevant molecular orbitals, according to Kivelson and Lee [11] are of the form

A_1: $\phi^*_{A1} (I) = \alpha^*_1(1/\sqrt{2}) (4s - 3d_Z^2) - \propto'^*_1 (\sigma_5),$

B_1: $\phi^*_{B1} = \beta^*_1 (3d_{X^2-Y^2}) - \beta'^*_1 (1/2) (\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4),$

B_2: $\phi^*_{B2} = \beta^*_2 (3d_{XY}) - \beta'^*_2 (1/2) (\pi_{X1}+\pi_{Y2} + \pi_{Y3} - + \pi_{X4}),$

E: $\phi^*_{E\pi} = \varepsilon^*_\pi (3d_{XZ}) - \varepsilon'^*_\pi (\pi_{X6})$

Or

$\phi^*_{E\pi} = \varepsilon^*_\pi (3d_{YZ}) - \varepsilon'^*_\pi (\pi_{Y6})$

$$(7)$$

where σ_i refers to a sp² ligand orbital on the ith ligand directed towards the ^{51}V nucleus, π_i 's are the ligand 2p orbitals directed along with i^{th} molecular axis. The β', α' and ε', are the coefficients of the ligand wavefunctions for bonding orbitals and β'^*, α'^* and ε'^* are the coefficients of the ligand wavefunctions for antibonding orbitals.

Table 1 The Spectral Parameters of V^{4+} in K_2O-B_2O_3-V_2O_5 Glasses, where mole % V_2O_5 / B_2O_3 =1

Sample	K_2O/B_2O_3 ratio	g_{II}	$g_{\perp}$	$| A_{II} |$ (10-4 cm^{-1})	$|A_{\perp}|$ (10^{-4}cm^{-1})	$\beta_2{}^*$	k
(1)	1.0	1.933	1.969	159	53	0.88	0.72
(2)	1.5	1.935	1.969	160	54	0.88	0.72
(3)	2.0	1.950	1.982	160	55	0.89	0.75
(4)	2.5	1.932	1.971	160	56	0.89	0.76
(5)	3.0	1.956	1.980	161	58	0.88	0.78

The values of $\beta_2{}^*$ and k are determined by using the experimental values of g and A tensors [determined by using eqs. (2) and (3)] in eqs. (4) and (5), where P = 0.0128 cm^{-1}, D_{II} = -0.0125 and $D_{\perp}$ = -0.0015, [3] and are listed in Table 1. The values of $\beta_2{}^*$ are in the range of 0.88-0.89 and show more or less same value for all samples. This result shows that the in-plane π bonding is somewhat covalent [see eq. (7), $\beta_2{}^*$ = 1 for ionic] and covalency is nearly independent of the concentration of K_2O.

The definition of contact coupling, k, is given by eq. (6) and this contact coupling can be interpreted by admixture of 4s character through configuration interaction or polarization [9]. From Table 1 it is seen that as the concentration of K_2O increases there is no significant change in values of g_{II} , $g_{\perp}$ and $\beta_2{}^*$ but values of k and A increase. Thus the slight increase of the A tensor in KBV glasses mainly arise from effects of k. The admixture is influenced by the energy separations of these levels. We would expect from eq. (7) that $A_1{}^*$ (I) energy is more strongly influenced by K_2O than other energies because k is interpreted by admixture of 4s character and 4s level belongs to the $A_1{}^*$ (I) energy [Eq. (7)]. This behaviour makes the g tensor constant and increases the A tensor slightly as K_2O is added. It is also observed that in-plane π bonding in the present potassium borovanadate glasses is more covalent in character than the vanadium doped alkali borate glasses [14].

Table 2 ESR Parameters of Various Vanadyl Complexes

System	g_{II}	$g_{\perp}$	$| A_{II} |$ (10-4cm-1)	$|A_{\perp}|$ (10-4cm-1)	Reference
VO2+ in borosilicate	1.936	1.976	172	60	9
VO2+ in LiCaB	1.934	1.976	172	65	8
VO2+ in LiMgB	1.932	1.975	168	60	8
VO2+ in LiBV	1.937	1.986	161	58	15
VO2+ in NaBV	1.941	1.988	160	58	15
VO2+ in K2SO4–ZnSO4	1.921	1.969	180	68	3
VO2+ in KBV	1.941	1.975	160	55	Present work

Hecht and Johnston [9] indicated the possibilities of threefold or fourfold symmetries to describe the crystal field of the V^{4+} ions in glasses. An octahedral site with a tetragonal compression would give g value in the order $g_{\parallel} < g_{\perp} < g_e$ (=2.0023). It is to be noted that the values observed in the present work confirm to this relationship and are close to those of the vanadyl complexes which are listed in Table 2. [3,8,15]. It is, therefore, suggested that the V^{4+} ions in the present samples exist as VO^{2+} ions in octahedral coordination with a tetragonal compression and belong to C_{4V} symmetry.

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