

Study of electron paramagnetic resonance in vanadyl doped tungsten lithium borate glasses

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Glasses with composition $x\text{WO}_3 \cdot (30-x)\text{Li}_2\text{O} \cdot 70\text{B}_2\text{O}_3$ containing 2 mol % V_2O_5 have been prepared over the range $0 \leq x \leq 15$ (x is in mol % and in steps of 2.5). The electron paramagnetic resonance (EPR) spectra of VO^{2+} in these glasses have been recorded on X-band ($\nu \approx 9.14$ GHz) at room temperature (RT). The spin Hamiltonian parameters, dipolar hyperfine coupling parameter, P and Fermi contact interaction parameter, K , have been calculated. It has been found that V^{4+} ions in these glasses exist as VO^{2+} in octahedral coordination with a tetragonal distortion. Results suggest that the tetragonality of the V^{4+}O_6 complex changes with change in $\text{WO}_3:\text{Li}_2\text{O}$ ratio. Values of theoretical optical basicity have also been calculated.

Keywords: Glasses, Borate glasses, Electron paramagnetic resonance, Vanadyl ion

1 Introduction

Electron paramagnetic resonance (EPR) spectroscopy is a sensitive technique for the study of transition metal (TM) ions in solids. It provides information concerning the valence state of TM ions, local environment and the nature of interactions between them. 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 surrounding cations are very sensitive¹. Vanadyl ion (VO^{2+}) has been used as a spectroscopic probe for characterization of glasses because their EPR spectra are rich in hyperfine structure due to ^{51}V nucleus and is easily observable at room temperature^{2,3}.

The present study has been carried out to observe the effect of substitution of lithium oxide with transition metal oxide (WO_3) on the microstructure around VO^{2+} in borate glasses.

2 Experimental Details

The glasses were prepared using the normal melt quenching method and AR grade chemicals LiCO_3 , WO_3 , H_3BO_3 and V_2O_5 . Approximately 15 g of chemicals were thoroughly mixed in porcelain crucible and then melted at 1473 K by using electrical furnace for about half an hour. The mixture was shaken frequently to ensure homogeneity. The glasses were obtained by pouring the melts onto a stainless steel plate pressed with another plate. First derivative

EPR spectra of the samples were recorded at room temperature (300K) in the X-band ($\nu \approx 9.14$ GHz) on an EPR spectrometer (Varian E-112). Magnetic field was modulated by 100 kHz. Polycrystalline DPPH was used as a standard g marker ($g=2.0036 \pm 0.0002$).

3 Results and Discussion

Fig. 1 shows the EPR spectra of the VO^{2+} in the present glasses. These spectra show features very similar to those found in various alkali borate glasses doped with vanadyl ion. The EPR spectra are having structures, which are characteristics of a hyperfine interaction arising from an unpaired electron with a ^{51}V nucleus having nuclear spin $7/2$.

The axial spin Hamiltonian used⁴ is 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 β is the Bohr magneton; g_{\parallel} and g_{\perp} are the parallel and perpendicular principal components of the g tensor; A_{\parallel} and A_{\perp} are the parallel and perpendicular principal components of hyperfine coupling tensor; B_x , B_y and B_z are the components of the magnetic field; and S_x , S_y , S_z and I_x , I_y , I_z are the components of spin operators of the electron and nucleus, respectively. The solutions of the spin Hamiltonian (1) are presented in Eqs (2) and (3) for the parallel and perpendicular orientations, respectively:

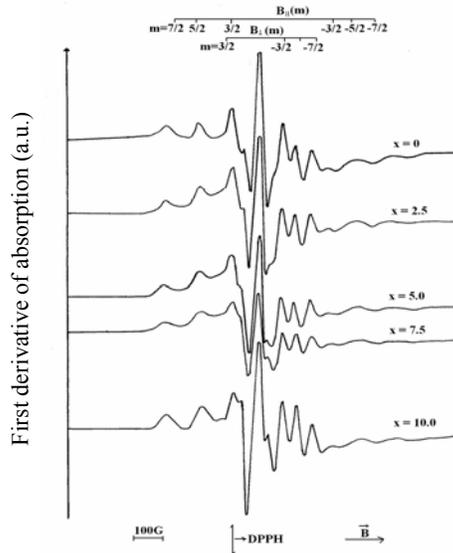


Fig. 1 — EPR spectra of VO^{2+} ion in $x\text{WO}_3 \cdot (30-x)\text{Li}_2\text{O} \cdot 70\text{B}_2\text{O}_3$ containing 2 mol % V_2O_5

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

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

where m is the magnetic quantum number of the vanadium nucleus, $B_{\parallel}(0) = h\nu/g_{\parallel}\beta$ and $B_{\perp}(0) = h\nu/g_{\perp}\beta$. Spin Hamiltonian parameters (SHP) of the VO^{2+} ion determined by using Eqs (2) and (3) for all samples are given in Table 1. The uncertainty in the value of g is ± 0.001 and in the value of A is $\pm 1.0 \times 10^{-4} \text{ cm}^{-1}$. 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 Lee⁵,

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

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

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. 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 electrons⁶ and the contribution to the hyperfine coupling due to the term $-PK$ is included. From the molecular orbital theory⁷, it can also be shown that the components A_{\parallel} and A_{\perp} consist of the

Table 1 — Spin Hamiltonian parameters of VO^{2+} at room temperature and A_{th} in $x\text{WO}_3 \cdot (30-x)\text{Li}_2\text{O} \cdot 70\text{B}_2\text{O}_3$ containing 2 mol % V_2O_5

Glass No. (x)	g_{\parallel} (± 0.0010)	g_{\perp} (± 0.0010)	A_{\parallel} (10^{-4} cm^{-1}) (± 1.0)	A_{\perp} (10^{-4} cm^{-1}) (± 1.0)	A_{th}
0	1.930	1.963	163.0	59.6	0.503
2.5	1.917	1.957	162.0	59.4	0.515
5.0	1.912	1.953	162.2	59.7	0.527
7.5	1.911	1.953	162.6	61.6	0.539
10.0	1.907	1.960	161.8	62.0	0.548
12.5	1.903	1.956	160.0	62.6	0.559
15.0	1.902	1.957	158.9	63.6	0.571

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 manner:

$$A_{\parallel} = -PK + A'_{\parallel} \dots (6)$$

$$A_{\perp} = -PK + A'_{\perp} \dots (7)$$

The values of A'_{\parallel} and A'_{\perp} were calculated and are given in Tables 1 and 2. The increase in the value of $\Delta g_{\parallel} / \Delta g_{\perp}$ indicates that the octahedral symmetry is reduced at V^{4+} ion site. The increase in the value of K is due to increase in tetragonality of V^{4+}O_6 complex. The decrease of the anisotropic contribution (i.e., $|A'_{\parallel}|$ and $|A'_{\perp}|$) of the $3d_{xy}$ electron to the hyperfine splitting is brought about by increasing 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 $\text{WO}_3 : \text{Li}_2\text{O}$ ratio.

The theoretical optical basicity serves in the first approximation as a measure of the ability of oxygen to donate a negative charge in the glass⁸. The theoretical optical basicity A_{th} for the present glass system is calculated by using the expression:

$$A_{th} = A_{\text{WO}_3} X_{\text{WO}_3} + A_{\text{Li}_2\text{O}} X_{\text{Li}_2\text{O}} + A_{\text{B}_2\text{O}_3} X_{\text{B}_2\text{O}_3} + A_{\text{V}_2\text{O}_5} X_{\text{V}_2\text{O}_5} \dots (8)$$

Table 2 — P , K , $|A'_{\parallel}|$, $|A'_{\perp}|$ and $\Delta g_{\parallel}/\Delta g_{\perp}$ of VO^{2+} in $x\text{WO}_3 \cdot (30-x)\text{Li}_2\text{O} \cdot 70\text{B}_2\text{O}_3$ containing 2 mol % V_2O_5

Glass No. (x)	P	K (10^{-4}cm^{-1})	$ A'_{\parallel} $ (10^{-4}cm^{-1})	$ A'_{\perp} $ (10^{-4}cm^{-1})	$\Delta g_{\parallel}/\Delta g_{\perp}$
0	113.0	0.782	74.7	28.8	1.837
2.5	110.9	0.785	74.9	27.7	1.861
5.0	109.3	0.789	74.3	26.5	1.896
7.5	108.1	0.814	73.5	26.2	1.958
10.0	106.7	0.833	72.9	26.2	2.051
12.5	103.6	0.853	71.5	25.8	2.115
15.0	99.3	0.895	68.1	23.2	2.206

where X_i 's and A_i 's are equivalent fractions and basicity of WO_3 , Li_2O , B_2O_3 and V_2O_5 . In other words the optical basicity is related to Lewis basicity of oxide glasses. Λ_{th} can be used to classify the covalent/ionic ratios of the glasses since an increasing Λ_{th} covalency between V^{4+} and oxygen ion should decrease, i.e. ability of oxygen to donate electron to V^{4+} should increase. This decreases the effective charge of V^{4+} nucleus and thus the $3d_{xy}$ expands which is consistent with the variation in the $|A'_{\parallel}|$, $|A'_{\perp}|$ and P .

4 Conclusions

The V^{4+} ions in vanadyl doped tungsten lithium borate glass samples exist as VO^{2+} ions in octahedral coordination with a tetragonal compression and belong to C_{4v} symmetry. Increase in the $\text{WO}_3 : \text{Li}_2\text{O}$ ratio results in an expansion of the $3d_{xy}$ orbit of unpaired electron in the vanadium ion. In tungsten lithium borate glasses samples, the spin Hamiltonian parameters (SHP) are in agreement with theoretical optical basicity, Λ_{th} .

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