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ESR of vanadyl ions in borate glasses

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The electron spin resonance (ESR) of VO^{2+} in $Li_2O-RO-B_2O_3$ (where R = Sr, Zn) glasses has been studied. Spin Hamiltonian parameters $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$, dipolar hyperfine coupling parameter P and Fermi contact interaction parameter K have been calculated. It is found that with a decrease in the percentage of B_2O_3 there is an improvement in the octahedral symmetry of the V^{4+} site. The theoretical optical basicity Λ_{th}, of the glasses has also been calculated.

1. Introduction

Some studies have been accumulated on the electron spin resonance (ESR) of transition metal ions in binary as well as ternary borate glasses [1–6]. Previously [6] we studied the ESR of VO^{2+} in $Li_2O-CdO-B_2O_3$ glasses and found that the tetragonality of the VO^{2+} ion decreases with a decrease in the percentage of B_2O_3, while the spin Hamiltonian parameters are almost constant within experimental error with the change in modifier content. We have now investigated the ESR of VO^{2+} in $Li_2O-RO-B_2O_3$ (where R = Sr, Zn) glasses. These glasses can be prepared [7] over a wide range of ternary composition.

2. Experimental procedure

In the present study samples were prepared using Analar grade reagents of H_3BO_3, Li_2CO_3, $SrCO_3$ and $ZnCO_3$ as starting materials. 1.0 mol % of V_2O_5 was added to each batch. Each batch was first sintered for about five hours at 600 ± 50° C and then melted in porcelain crucibles in an electric muffle furnace. The melt was poured on to one carbon plate and pressed with another. The compositions of the samples are shown in Table I.

First-derivative ESR spectra were recorded at room temperature (295 K) in the X-band (~ 9.3 GHz) on an ESR spectrometer (Varian E 109). Samples were glued to a quartz rod 4 mm in diameter inside a rectangular cavity (Varian E-231 multipurpose cavity) operating in the TE_{102} mode ($Q \sim 7000$). Magnetic field was measured with a digital fluxmeter (Varian E-500). A magnetic field modulation of 100 kHz with peak-to-peak amplitude of 0.1 mT was applied. Polycrystalline DPPH was used as a standard g marker ($g = 2.0036 \pm 0.0002$). ESR spectra of some of these samples were also recorded at liquid nitrogen temperature (LNT) where the spectra were found to be virtually identical to those at room temperature.

3. Results and discussion

The ESR spectra of glasses S3, S5, S10, S13 and Z3, Z5, Z10, Z13 are shown in Figs 1 and 2, respectively. The spectra obtained for these glasses are similar to the spectra obtained for various borate glasses [1, 5] and show characteristic curves of a hyperfine interaction of the unpaired electron with a V^{51} nucleus having spin $\frac{7}{2}$.

The spectra could best be analysed using an axial spin Hamiltonian [8, 9] with solutions for the parallel

TABLE I Glasses studied in $x Li_2O \cdot Y RO \cdot (100 - x - y)B_2O_3$ system (where R = Sr, Zn)

$x Li_2O \cdot Y SrO(100 - x - y)B_2O_3$			$x Li_2O \cdot Y ZnO(100 - x - y)B_2O_3$		
Glass No.	x	y	Glass No.	x	y
S1	5	10	Z1	5	10
S2	7	8	Z2	7	8
S3	10	5	Z3	10	5
S4	6	13	Z4	6	13
S5	10	9	Z5	10	9
S6	13	6	Z6	13	6
S7	10	15	Z7	10	15
S8	12	13	Z8	12	13
S9	15	10	Z9	15	10
S10	10	20	Z10	10	20
S11	15	15	Z11	15	15
S12	20	10	Z12	20	10
S13	10	25	Z13	10	25
S14	15	20	Z14	15	20
S15	25	10	Z15	25	10

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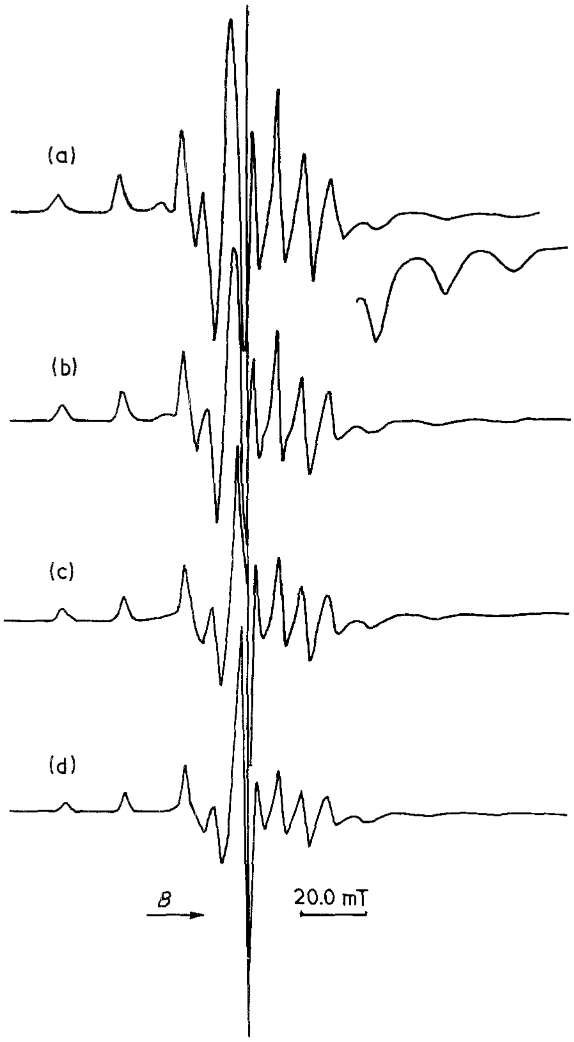

Figure 1 The ESR spectra of VO^{2+} ions in Li_2O–SrO–B_2O_3 glasses (Table I) in the X-band (~ 9.3 GHz) at 295 K: (a) S3, (b) S5, (c) S10, (d) S13. Spectrum below (a) is for S3 with ten times increase in gain.

and perpendicular components [9, 10] as

$$B_{\parallel}(m) = -mA_{\parallel}(1 + P') + B_{\parallel}(0) \times \{1 - 4P'[I(I + 1) - m^2(1 + P')]\}^{1/2} \quad (1)$$

$$B_{\perp}(m) = -mA_{\perp}(1 + P_1) + B_{\perp}(0) \times \{1 - 4P_1[I(I + 1) - m^2(1 + P_1)]\}^{1/2} - \frac{(A_{\parallel} - A_{\perp})^2}{8B_{\perp}(0)}[I(I + 1) - m^2] \quad (2)$$

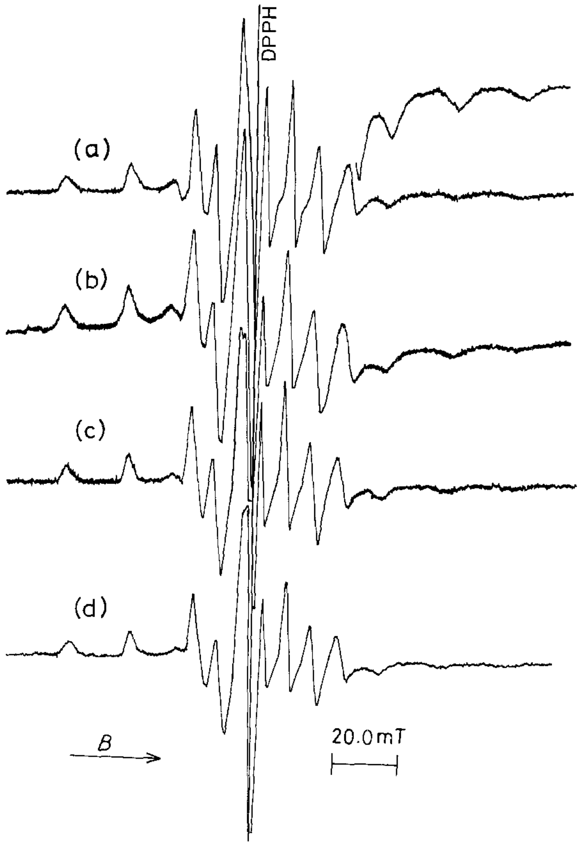

Figure 2 The ESR spectra of VO^{2+} ions in Li_2O–ZnO–B_2O_3 glasses (Table II) in the X-band (~9.3 GHz) at 295 K: (a) Z3, (b) Z5, (c) Z10, (d) Z13. Spectrum above (a) is for Z3 with ten times increase in gain.

with

$$P' = \frac{A_{\perp}^2}{4B_{\parallel}^2(0) - A_{\parallel}^2}$$

$$P_1 = \frac{(A_{\parallel} + A_{\perp})^2}{4[4B_{\perp}^2(0) - A_{\perp}^2]}$$

where m is the magnetic quantum number of the vanadium nucleus; $B_{\parallel}(0) = h\nu/g_{\parallel}\beta$ and $B_{\perp}(0) = h\nu/g_{\perp}\beta$.

Equations 1 and 2 were used to determine the spin Hamiltonian parameters of the VO^{2+} ion and are given in Tables II and III. The uncertainty in the value of g is ± 0.0015 and in the value of A is $\pm 0.8 \times 10^{-4}\,cm^{-1}$. Calculated values [11] of the dipolar

TABLE II Spin Hamiltonian parameters P and K of VO^{2+} in Li_2O–SrO–B_2O_3 glasses at 295 K

Glass No.	$g_{\parallel}$	$g_{\perp}$	$\lvert A_{\parallel}\rvert$ ($10^{-4}\,cm^{-1}$)	$\lvert A_{\perp}\rvert$ ($10^{-4}\,cm^{-1}$)	P	K
S1	1.9398	1.9819	176.0	65.7	120.87	0.8132
S2	1.9392	1.9813	176.5	65.7	121.47	0.8098
S3	1.9397	1.9824	173.9	63.9	120.55	0.7998
S4	1.9338	1.9742	174.2	62.7	121.87	0.7778
S5	1.9404	1.9778	172.1	60.9	122.15	0.7653
S6	1.9391	1.9801	174.7	64.7	120.59	0.8048
S7	1.9399	1.9730	170.7	59.9	121.93	0.7537
S8	1.9384	1.9772	172.5	61.2	122.0	0.7676
S9	1.9461	1.9803	170.8	61.3	120.96	0.7751
S10	1.9429	1.9728	169.7	58.7	122.58	0.7411
S11	1.9395	1.9749	171.7	61.1	121.46	0.7675
S12	1.9441	1.9795	171.2	59.3	123.29	0.7490
S13	1.9440	1.9725	167.9	57.1	122.46	0.7286
S14	1.9432	1.9731	168.8	57.1	123.34	0.7258
S15	1.9439	1.9713	168.2	57.1	122.94	0.7254

TABLE III Spin Hamiltonian parameters P and K of VO^{2+} in Li_2O–ZnO–B_2O_3 glasses at 295 K

Glass No.	$g_\parallel$	$g_\perp$	$\lvert A_\parallel \rvert$ (10^{-4} cm^{-1})	$\lvert A_\perp \rvert$ (10^{-4} cm^{-1})	P	K
Z1	1.9373	1.9794	177.5	67.5	120.33	0.8290
Z2	1.9373	1.9794	177.5	67.5	120.33	0.8290
Z3	1.9358	1.9788	176.6	68.4	118.28	0.8452
Z4	1.9397	1.9797	177.5	67.5	120.69	0.8270
Z5	1.9392	1.9797	176.5	67.5	119.58	0.8321
Z6	1.9355	1.9777	175.5	65.8	119.92	0.8152
Z7	1.9423	1.9800	174.4	64.2	121.18	0.7978
Z8	1.9394	1.9771	174.1	64.1	120.76	0.7965
Z9	1.9388	1.9753	173.0	64.0	118.38	0.8054
Z10	1.9440	1.9812	173.5	63.3	121.37	0.7905
Z11	1.9428	1.9788	173.3	62.3	122.25	0.7767
Z12	1.9397	1.9739	172.2	61.3	121.84	0.7669
Z13	1.9396	1.9756	171.3	60.9	121.30	0.7665
Z14	1.9421	1.9753	171.5	61.3	121.44	0.7689
Z15	1.9448	1.9768	170.2	59.5	123.06	0.7520

TABLE IV $A'_\parallel$, $A'_\perp$, PK, $\Delta g_\parallel/\Delta g_\perp$ of VO^{2+} and Λ_{th} of Li_2O–SrO–B_2O_3 glasses at 295 K

Glass No.	$\lvert A'_\parallel \rvert$ (10^{-4} cm^{-1})	$\lvert A'_\perp \rvert$ (10^{-4} cm^{-1})	PK (10^{-4} cm^{-1})	$\Delta g_\parallel/\Delta g_\perp$	Λ_{th}
S1	77.67	32.60	98.29	3.0637	0.4540
S2	78.13	32.70	98.37	3.0048	0.4540
S3	77.46	32.55	96.41	3.1457	0.4540
S4	79.45	32.12	94.79	2.4377	0.4638
S5	78.64	32.54	93.48	2.5265	0.4638
S6	77.67	32.34	97.05	2.8468	0.4638
S7	78.82	32.03	91.90	2.1297	0.4797
S8	78.83	32.45	93.65	2.5458	0.4797
S9	77.05	32.47	93.76	2.5545	0.4797
S10	78.87	32.17	90.84	2.0135	0.4942
S11	78.46	32.09	93.22	2.2920	0.4942
S12	78.84	33.01	92.34	2.5526	0.4942
S13	78.68	32.12	89.22	1.9564	0.5099
S14	79.31	32.41	89.52	2.0240	0.5099
S15	79.07	32.12	89.18	1.8839	0.5099

hyperfine coupling parameter P and the Fermi contact interaction term K are also given in Tables II and III. Further hyperfine tensor components, $A_\parallel$ and $A_\perp$, consist [12] of the contributions $A'_\parallel$ and $A'_\perp$ of 3dxy electron to the hyperfine structure and the PK term arising from anomalous contribution of the s-electrons. In Tables IV and V are given the calculated values of $A'_\parallel$, $A'_\perp$ and PK along with the calculated value of $\Delta g_\parallel/\Delta g_\perp$. It can be seen from Tables II to V that there are some unmistakable trends apparent in the spin Hamiltonian parameters. $g_\parallel$ increases while $g_\perp$, $A_\parallel$, $A_\perp$, K, PK and $\Delta g_\parallel/\Delta g_\perp$ decrease with a decrease in the percentage of B_2O_3. The value of P increases slightly while $A'_\parallel$ and $A'_\perp$ are almost constant within experimental error. The decrease in the value of $\Delta g_\parallel/\Delta g_\perp$ indicates a decrease in covalency or tetragonal distortion [13] along the V^{4+}–O (vanadyl) bond. Smaller values of K also suggest [4, 13] a decrease of the tetragonality of the $V^{4+}O_6$ complex because of a strongly bonded oxygen atom at the V^{4+} ion, in the

TABLE V $A'_\parallel$, $A'_\perp$, PK, $\Delta g_\parallel/\Delta g_\perp$ of VO^{2+} and Λ_{th} of Li_2O–ZnO–B_2O_3 glasses at 295 K

Glass No.	$\lvert A'_\parallel \rvert$ (10^{-4} cm^{-1})	$\lvert A'_\perp \rvert$ (10^{-4} cm^{-1})	PK (10^{-4} cm^{-1})	$\Delta g_\parallel/\Delta g_\perp$	Λ_{th}
Z1	77.77	32.20	99.75	2.8384	0.4391
Z2	77.77	32.20	99.75	2.8384	0.4425
Z3	76.64	31.61	99.97	2.8298	0.4475
Z4	77.68	32.34	99.81	2.7699	0.4437
Z5	77.05	32.03	99.50	2.7920	0.4500
Z6	77.79	31.95	97.76	2.7154	0.4385
Z7	77.68	32.50	96.68	2.6906	0.4543
Z8	77.91	32.10	96.18	2.4960	0.4579
Z9	77.61	31.31	95.34	2.3518	0.4633
Z10	77.53	32.65	95.94	2.7630	0.4582
Z11	78.37	32.66	94.95	2.5319	0.4676
Z12	78.74	32.10	93.44	2.2042	0.4770
Z13	78.29	32.11	92.98	2.3483	0.4624
Z14	78.12	32.11	93.37	2.2296	0.4722
Z15	77.63	33.08	92.54	2.2550	0.4918

site opposite the vanadyl oxygen. Tables II to V show that there is no significant change in the spin Hamiltonian parameters with the change in modifier content while keeping B_2O_3 constant.

The theoretical optical basicity (Λ_{th}) has also been calculated using the expression [14]

$$\Lambda_{th} = \sum_i \frac{Z_i r_i}{2\gamma_i} \qquad (3)$$

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

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

where x_i the Pauling electronegativity [15] of the cation. Values of the optical basicity thus calculated are given in Tables IV and V; it may be noted that $g_\parallel$ increases while $g_\perp$, $A_\parallel$, $A_\perp$, K and $\Delta g_\parallel/\Delta g_\perp$ decrease with increase in Λ_{th} while keeping Li_2O constant. It can also be seen from Table IV that in Li_2O–SrO–B_2O_3 glasses, at a constant percentage of B_2O_3 with varying modifier content, the change in spin Hamiltonian parameters is independent of the change in Λ_{th}. Klonkowski [16] also observed an insignificant change in the ESR parameters of Cu^{2+} with increasing optical basicity.

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