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

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Glasses with composition xWO3.(30-x)Li2O.70B2O3 containing 2 mol % V2O5 have been prepared over the range 0 ≤ x ≤ 15 (x is in mol % and in steps of 2.5). The electron paramagnetic resonance (EPR) spectra of VO2+ in these glasses have been recorded on X-band (ν ≈ 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 V4+ ions in these glasses exist as VO2+ in octahedral coordination with a tetragonal distortion. Results suggest that the tetragonality of the V4+O6 complex changes with change in WO3:Li2O 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 sensitive. Vanadyl ion (VO2+) 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.

The present study has been carried out to observe the effect of substitution of lithium oxide with transition metal oxide (WO3) on the microstructure around VO2+ in borate glasses.

2 Experimental Details

The glasses were prepared using the normal melt quenching method and AR grade chemicals LiCO3, WO3, H3BO3 and V2O5. 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 (ν=9.14GHz) on an EPR spectrometer (Varian E-112). Magnetic field was modulated by 100 kHz. Polycrystalline DPPH was used as a standard $g$ marker ($g=2.0036±0.0002$).

3 Results and Discussion

Fig. 1 shows the EPR spectra of the VO2+ 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 used is of the form

$$ H = \beta g_\parallel B_x S_x + \beta g_\perp (B_x S_x + B_y S_y) + A_\parallel S_x I_x + A_\perp (S_x I_x + S_y I_y) \quad \ldots (1) $$

where $\beta$ 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.
using the expressions developed by Kivelson and the Fermi contact interaction term, shown that the components

where

and

determined by using Eqs (2) and (3) for all samples containing 2 mol % V₂O₅.

From the molecular orbital theory, it can also be shown 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 manner:

\[
A_{\parallel} = -PK + A'_{\parallel} \quad \text{...(6)}
\]

\[
A_{\perp} = -PK + A'_{\perp} \quad \text{...(7)}
\]

The values of \( A'_{\parallel} \) and \( A'_{\perp} \) were calculated and are given in Tables 1 and 2. The increase in the value of \( A'_{\parallel} / A_{\parallel} \) 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 WO\(_3\) : Li\(_2\)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 glass. The theoretical optical basicity \( A_{\text{th}} \) for the present glass system is calculated by using the expression:

\[
A_{\text{th}} = A_{\text{WO3}}X_{\text{WO3}} + A_{\text{Li2O}}X_{\text{Li2O}}
\]

\[
+ A_{\text{B2O3}}X_{\text{B2O3}} + A_{\text{V2O5}}X_{\text{V2O5}} \quad \text{...(8)}
\]

<table>
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<th>Glass No.</th>
<th>( g_{\parallel} ) (±0.0010)</th>
<th>( g_{\perp} ) (±0.0010)</th>
<th>( A_{\parallel} ) (10(^{-4}) cm(^{-1})) (±1.0)</th>
<th>( A_{\perp} ) (10(^{-4}) cm(^{-1})) (±1.0)</th>
<th>( A_{\text{th}} )</th>
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<td>163.0</td>
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<td>59.4</td>
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The first derivative of absorption (a.u.)

Fig. 1 — EPR spectra of VO\(^{2+}\) ion in xWO\(_3\). (30-x)Li\(_2\)O.70B\(_2\)O\(_3\) containing 2 mol % V\(_2\)O\(_5\).
4 Conclusions

The V⁴⁺ ions in vanadyl doped tungsten lithium borate glass samples exist as VO²⁺ ions in octahedral coordination with a tetragonal compression and belong to C₄ᵥ symmetry. Increase in the WO₃ : Li₂O ratio results in an expansion of the 3dₓᵧ 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, Λₖ.

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References