EPR studies on VO$^{2+}$doped sodium –borate glasses synthesized by microwave method

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ABSTRACT
Electron paramagnetic resonance (EPR) of VO$^{2+}$ions in sodium borate glass system has been studied over a wide range of composition. The EPR spectra exhibited hyper fine splitting (hfs) due to considerable weakening of interaction between vanadium ion concentrations. The hfs is seen between 10 and 35 mol% of vanadium concentration. The appearance of hfs is due to the interaction of 3$d^1$ electron spin of $^{51}$V ion with its nuclear spin, which increases with increasing concentration till 35 mol%. The spin -Hamiltonian parameters ($g$ and $A$), the dipolar hyperfine coupling parameter ($P$) and Fermi contact interaction parameter ($k$) have also been evaluated. The values of spin-Hamiltonian parameters indicate that VO$^{2+}$ ions are in octahedral coordination with a tetragonal compression which can be attributed to the structural changes taking place with the increasing concentration of $V_2O_5$.

Key words: Glasses, Electron paramagnetic resonance, hyper fine splitting, octahedral coordination.

1. INTRODUCTION
Glasses are a class of amorphous materials exhibiting a variety of useful properties which can be used for technological applications. These materials were extensively synthesized by conventional melt quenching method. In this method thermal energy is delivered to the surface of the material, thus thermal gradient will develop in the long heating process and material loss may occur. However, in microwave heating uniform and volumetric heating of the material takes place. Since microwave heating is faster and energy efficient, we adopted this method to prepare the samples. Glasses containing transition metal ions have attracted researchers due to their physical applications in electronic and electro-optic devices [1,2].Vanadium pentoxide based materials have been used as cathode materials in alkali batteries [3,4].These materials are suitable for electrochemical properties because the electrochemical redox potential of $V^{5+}$-$V^{4+}$ couple as compared to the Li$^+$/Li couple is high as lithium glasses offers sufficiently high Li$^+$ diffusion coefficient.Glasses containing $V_2O_5$ are of interest for studying the correlation between electrical properties and changes in the glass network because $V_2O_5$ is unique, being itself, a conditional glass former. In amorphous $V_2O_5$, the closest site spacing between $V$ – $V$ is about 3.5 Å, a value which is almost equal to twice the value of $V$ – $O$ spacing [1.75 Å] in the basic structural unit and which corresponds to the $O$ – $V$ – $O$ distance of the basal plane. Thus, the glass structure optimizes the packing of such units. The basic borovanadate glasses consists of trigonal [BO$_2$]$^5$ and tetrahedral [VOO$_2$]$^6$ units. During modification, it is important to decide which of [BO$_2$]$^5$ and [VOO$_2$]$^6$ units modify preferentially. The preference of modification is decided by the Sandersons electronegativity principle [5]. Since both the structural units [BO$_2$]$^5$ and [VOO$_2$]$^6$ have the same electronegativity, they have equal a priory probability to interact with the oxide ion.

Electron Paramagnetic Resonance (EPR) spectroscopy is one of the sensitive and important spectroscopic technique to study paramagnetic centers of transition metal ions. There are classic review reports on EPR technique [6,7]. The applicability of the EPR technique to $V_2O_5$ containing glass system is mainly due to the presence of $V^{4+}$ paramagnetic centers, whose outer shell structures, 3$p^6$, 3$d^1$ enables unpaired magnetic moment of 3$d^1$ electron to interact with the applied field. Since a
V\(^{4+}\) ion has an electronic spin $s = 1/2$, a nuclear spin $I = 7/2$ leading to the interactions between corresponding magnetic moments resulting in a hyperfine structure [8, 9]. At lower concentrations of V\(_2\)O\(_5\) hyperfine structure is seen in all the spectra typical of V\(^{4+}\) (isolated) ions. With increasing V\(_2\)O\(_5\) concentration, hyperfine structure was superposed by a broad signal without showing any hyperfine structure characteristic of clustered ions. Gupta et al [10] pointed out that, long range spin-spin interactions between V\(^{4+}\) ions and the spin orbit coupling cause an anisotropy of the $g$-factor and the broadening of the individual lines [11]. In glasses only orientation averaged spectra can be observed, that leads to additional reduction of hyperfine structure lines. It was seen in V\(_2\)O\(_5\)-TeO\(_2\) glasses that, the disappearance of hyperfine structure lines at higher contents of V\(_2\)O\(_5\) is due to superexchange interaction of V\(^{4+}\)-O-V\(^{5+}\)linkages [12]. In this paper we attempted to study EPR spectra of microwave synthesized glasses doped with vanadyl ions.

2. EXPERIMENTAL

Glasses were prepared by using the general formula $x$ V\(_2\)O\(_5\)· $(100 - x) [0.5\text{Na}_2\text{O} : \text{B}_2\text{O}_3]$ (where $x = 10, 15, 20, 25, 30, 35$ mol %) by microwave melting technique using analytical grade sodium carbonate, orthoboric acid, and vanadium pentoxide as starting materials. Appropriate quantity of weighed chemicals were mixed and thoroughly ground to homogenize the mixture and kept in a silica crucible inside a domestic kitchen microwave oven operating at 2.45 GHz, 850 W for about 3 to 5 minutes. Glass was obtained by rapidly quenching the melt between two copper blocks preheated to 100°C to avoid cracking of the samples. Glasses were annealed in a muffle furnace for about 2 hours at 200°C to remove thermal strains that could have developed during fast quenching.

Electron paramagnetic resonance spectra have been recorded on an EPR spectrometer (JEOL FE1X) operating in the X-band frequency (9.205 GHz) with a modulation frequency of 100 kHz. The magnetic field was scanned from 2200 to 4200 G with a scan speed of 625 G/min and the microwave power used was 5 mW. A powdered glass specimen of 100 mg was taken in a quartz tube for EPR measurements. The EPR spectrum of CuSO\(_4\)-5H\(_2\)O powdered sample was also recorded as a reference to calculate the number of spins. Polycrystalline DPPH with an effective $g$ value of 2.0023 was used as a standard field marker.

3. RESULTS AND DISCUSSION

3.1. EPR spectroscopic studies

EPR is a technique which provides information comprising the valence states of transition metal ions (TMI), local environment and nature of interaction between them. The EPR spectra exhibited hyperfine structure (hfs) due to considerable weakening of interaction between vanadium ion concentration. The EPR spectra of vanadyl ions [VO\(^{5+}\)] in glasses are very interesting because the valance state of vanadyl ions in glasses changes with the glass composition. The presence or absence of hfs in the EPR spectra is due to the modification of the glass structure caused by the modifier oxide (Na\(_2\)O). Fig.1 illustrates EPR spectra of sodium boro-vanadate glasses. EPR spectrum consisting of eight lines corresponding to eight values of nuclear magnetic quantum numbers $m = -7/2, -5/2, \ldots, +7/2$. The hfs is seen between 10 and 35 mol% of V\(_2\)O\(_5\). The appearance of hfs is due to the interaction of 3d\(^5\) electron spin of \(5\) V ion with its nuclear spin, which increases with increasing concentration till 35mol% which is evident from Fig.1. The disappearance of hfs for V\(_2\)O\(_5\)concentrations above 40 mol% can be attributed to an enhanced electron hopping between aliovalent vanadium centers along V\(^{4+}\) – O – V\(^{5+}\)linkages. Short life time of 3d\(^1\) electron on V\(^{4+}\) center causes the broadening of the energy levels of hfs and consequently leads to its disappearance.

It can be seen from Fig.1, a strong absorption line arises from the fact that at high V\(_2\)O\(_5\) content, most of the vanadium ions are in the V\(^{4+}\) state. The absence of hyperfine structure (hfs) points to the interaction between vanadium centers via V\(^{4+}\)-O-V\(^{5+}\)superexchange mechanism. Generally, such glasses exhibit electronic conductivity [13]. At 35 mol% of vanadium, the EPR spectra consists of V\(^{4+}\) line with a weak but visible superimposed hfs, which indicates the cross-over from hfs regime to non-hfs regime. However, the mechanism of conduction in glasses with high concentration of V\(_2\)O\(_5\) has been suggested as the transfer of an electron from V\(^{4+}\) site to V\(^{5+}\) site. Structural groups formed in V\(_2\)O\(_5\) rich glasses, provide the path for hopping of electrons. The increase in V\(_2\)O\(_5\) rich glasses can be
explained by considering the decrease in average distance between the TMI site and redox ratio.

The EPR spectra is well resolved from x = 10 to 35mol% due to $^{51}\text{V}$ and interpreted using axially symmetric spin Hamiltonian [14]. The solutions of the spin Hamiltonian are given by the following equations:

\[
B_\parallel(m) = B_\parallel(0) - m A_\parallel - \left[ \frac{63}{4} - m^2 \right] \frac{A_\parallel^2}{2B_\parallel(0)}
\]

\[
B_\perp(m) = B_\perp(0) - m A_\perp - \left[ \frac{63}{4} - m^2 \right] \frac{A_\parallel A_\perp + A_\perp^2}{4B_\perp(0)}
\]

where \( m \) is the magnetic quantum number, \( \nu \) is the frequency of the spectrometer, \( h \) is the Planck’s constant, \( \beta \) is the Bohr magneton, \( B \) is the magnetic field, \( g \) and \( A \) are the spin-Hamiltonian parameters.

Also, \( B_\parallel(0) = \frac{\hbar \nu}{g_\parallel \beta} \) and \( B_\perp(0) = \frac{\hbar \nu}{g_\perp \beta} \)

\( A_\parallel \) and \( A_\perp \) have been computed using the relations

\[
A_\parallel = \frac{1}{7} \left[ B_\parallel(\frac{-7}{2}) - B_\parallel(\frac{7}{2}) \right]
\]

\[
A_\perp = \frac{1}{7} \left[ B_\perp(\frac{-7}{2}) - B_\perp(\frac{7}{2}) \right]
\]

The spin Hamiltonian parameters \( g_\parallel, g_\perp, A_\parallel \) and \( A_\perp \) have been calculated and the values are listed in Table 1. Fig.2 show the variation of \( A_\parallel \) and \( A_\perp \) with \( \text{V}_2\text{O}_5 \) mol%. As can be seen from Fig.2 that both \( A_\parallel \) and \( A_\perp \) gradually decreases with increasing \( \text{V}_2\text{O}_5 \) content, which suggests that the covalence between the central atom and the surrounding oxygen ligands.

![Figure 1: EPR spectra obtained at room temperature for NBV glass system with varying mol% of \text{V}_2\text{O}_5 and identical mol% of NaO and B_2O_3](image)

![Figure 2: Variation of $A_\parallel$ and $A_\perp$ with \( \text{V}_2\text{O}_5 \) mol% in NBV glass system](image)
It is clear from Table 1, that the values of $g_\perp$ increases while $g_\parallel$ decreases with increasing V$_2$O$_5$ concentration suggesting a greater tetragonal distortion of vanadyl complex. Further, the value of $g_\perp > g_\parallel$ suggesting that vanadium present in glass as vanadylion[VO$^{2+}$] at a tetragonally distorted octahedral site [15].

It has been qualitatively shown from molecular orbital theory that $A_\parallel$ and $A_\perp$ consists of contribution from 3d$_{xy}$ electrons and anamolus contributions from the s- electrons. The variation of anamolous contributions $A'_\parallel$ and $A'_\perp$ with V$_2$O$_5$ mol% are shown in Fig. 3.

$A'_\parallel$ and $A'_\perp$ were calculated using the values of $A_\parallel$, $A_\perp$, P and k. The dipolar coupling constant (P) and fermi – contact coupling parameter ($k$) are evaluated using the expression given by Kivelson and Lee [16],

$$ A_\parallel = -P\left[k + \frac{4}{7} - \Delta g_\parallel - \frac{3}{7} \Delta g_\perp \right] $$

$$ A_\perp = -P\left[k - \frac{2}{7} - \frac{11}{14} \Delta g_\perp \right] $$

where $g_e = 2.0023$, $\Delta g_\parallel = g_\parallel - g_e$ and $\Delta g_\perp = g_\perp - g_e$. The values of P and k evaluated using the relations (5) and (6) are presented in Table 1. Equation (5) and (6) can be written as

$$ A'_\parallel = A'_\parallel - P\beta^2k $$

$$ A'_\perp = A'_\perp - P\beta^2k $$

The hyperfine components of $A_\parallel$ and $A_\perp$ consists of the contributions of $A'_\parallel$ and $A'_\perp$ of the 3d$_{xy}$electrons to the hyperfine structures. It is evident from Fig. 3 that both $A'_\parallel$ increases and $A'_\perp$ decreases with increasing concentration of V$_2$O$_5$, indicating that as V$_2$O$_5$ content increases the V – O bond becomes more covalent and 3d$_{xy}$orbitals are dilated. Assuming the free electron g- value (2.0023), $\Delta g_\parallel$ and $\Delta g_\perp$ are calculated. It can be seen from Table .1 that the ratio $\frac{\Delta g_\parallel}{\Delta g_\perp}$ increases with increasing V$_2$O$_5$ concentration. Besides, the ratio $\frac{\Delta g_\parallel}{\Delta g_\perp}$ is a measure of the degree of teragonality. The values of g -tensor depends on distortion type. In general, the axial distortion can be either three fold or four fold symmetries to describe the crystal field of V$^{4+}$ions in glasses. The bonding of the vanadyl ion in ligand field of octahedral symmetry has been well characterized by earlier workers [17-19].

The V$^{4+}$ site in the VO$^{2+}$ ion forms planar bonds with each of the four oxygen ligands. VO$^{2+}$ is an octahedral environment of oxygen with tetrahedral distortion (C$_{4v}$) where the vanadyl oxygen forms the apex V–O bond. Pk$/\gamma$ is evaluated using $\gamma$ the gyromagnetic ratio which is equal to 1.468 for $^{51}$ V. The variation of P and k with V$_2$O$_5$ concentration is shown in Fig. 4 while that of $Pk/\gamma$ versus V$_2$O$_5$ mol % is shown in Fig. 5.
The variations seen in these parameters indicate the s-character of the magnetic spin of V$_2$O$_5$, which arises due to the partial unpairing or polarization of s-electrons as a result of an interaction with unpaired d-electron [20]. $P_k$/$\gamma$ is found to increase with increasing concentration of V$_2$O$_5$, indicating an increase in tetragonal distortion and is also a measure of ‘s’ character of the spin of the vanadium. The bonding coefficient $\alpha^2$ can be evaluated using the relation [21].

$$\alpha^2 = \left[1 - \frac{g_{\parallel}}{g_e}\right] \frac{E}{4\lambda^2\beta^2} m$$  \hspace{1cm} \text{(9)}

where $E$ is the energy of the transition [$^2B_2$ - $^2B_1$] and $\beta^2$ is a measure of the in-plane $\pi$-bonding with the equilateral ligand and $\lambda$ is the spin orbit coupling constant and is equal to 170 cm$^{-1}$. The value of $\alpha^2$ calculated using the relation (9) is given in Table 2.

4. CONCLUSIONS

The spin Hamiltonian parameters extracted from the spectra shows that vanadium ions are present in the matrix of glass as a vanadyl [VO$_5^+$] complex. A – tensor, $g$- tensor, dipolar hyperfine coupling parameter (P) and Fermi – contact coupling parameter ($k$) exhibit composition dependent trend. Increase in V$_2$O$_5$ concentration greatly affects the tetragonal distortion of the vanadyl complex. From EPR studies, it can be concluded that the tetrahedral vanadium ions in the investigated glasses exist in vanadyl complexes with the tetragonally distorted octahedral sites.

**Table:1 Spin Hamiltonian parameters of VO$_{2+}$ ion in glass system.**

| Code       | $g_{\parallel}$ | $g_{\perp}$ | $\Delta g_{\parallel}$ | $\Delta g_{\perp}$ | $\Delta g_{\parallel}/\Delta g_{\perp}$ | $A_{\parallel}$ | $A_{\perp}$ | P | $k$  | $P_k/\gamma$ |
|------------|-----------------|------------|-------------------------|---------------------|------------------------------------------|-----------------|-------------|---|-----|----------------|
| NBV1(10V)  | 1.962           | 1.970      | 0.0430                  | 0.0320              | 1.26                                     | 163            | 54          | 131| 0.72| 0.0064              |
| NBV2(15V)  | 1.959           | 1.978      | 0.0433                  | 0.0243              | 1.78                                     | 168            | 55          | 133| 0.73| 0.0067              |
| NBV3(20V)  | 1.956           | 1.980      | 0.0463                  | 0.0223              | 2.07                                     | 169            | 60          | 134| 0.74| 0.0068              |
| NBV4(25V)  | 1.955           | 1.982      | 0.0473                  | 0.0203              | 2.33                                     | 174            | 62          | 137| 0.75| 0.0070              |
| NBV5(35V)  | 1.954           | 1.985      | 0.0483                  | 0.0173              | 2.79                                     | 177            | 64          | 138| 0.76| 0.0071              |

**Table: 2 Molecular orbital coefficients and crystal field splitting parameters.**

| Code       | $\lambda$ | $\Delta_{\parallel}$ | $\beta^2$ | $\alpha^2$ |
|------------|-----------|-----------------------|-----------|------------|
| NBV3(30V)  | 482       | 20746                 | 0.7367    | 0.7207     |
| NBV2(20V)  | 477       | 20964                 | 0.7137    | 0.7128     |
| NBV1(10V)  | 473       | 21141                 | 0.6264    | 0.6257     |

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