CHAPTER 4
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SPECTROSCOPIC STUDIES ON VANADYL ION DOPED IN MIXED ALKALI CADMIUM PHOSPHATE GLASSES

4.1 INTRODUCTION

Spectroscopic techniques such as Optical Absorption and Electron Paramagnetic Resonance (EPR) are prevailing tools for better understanding of the nature of energy levels of the transition metal ions in solids. The present investigations are undertaken with a view to understand the nature and cause of the splittings of energy levels of the transition metal ions in solids. In this, the results of the optical absorption and EPR studies on the vanadyl ion VO$^{2+}$ in mixed alkali phosphate glasses are presented.

Vanadium is the nineteenth most abundant element by weight in the earth's crust and is the fifth most abundant transition element. It has been extensively used as a probe to understand the phosphate glass system through its characteristic optical and EPR spectra. In its tetravalent state, Vanadium exists almost exclusively as the Vanadyl ion VO$^{2+}$ which is formed when the V$^{4+}$ with a single unpaired 3d electron is bound to an Oxygen by strong covalent bond. According to Selbin [1], this species is the most stable diatomic radical. The ESR spectrum of V$^{4+}$ in glasses is rich in hyperfine structure due to the $^{51}$V nucleus (I = 7/2) and is easily
observable in most systems at room temperature. The number of hyperfine lines observable is equal to \((2I+1)\) eight.

The Vanadyl ion \((\text{VO}^{2+})\) incorporated in glasses has been studied in order to characterize the local structure of glasses [2-11] and the changes caused by the mixed alkali variation as well as to obtain information about the local symmetry around the metallic ions [12-26]. In the present work, the influence of the \(\text{V}_2\text{O}_5\) on the local symmetry and interaction between vanadium ions through the mixed alkali variation in cadmium phosphate glasses are investigated by Optical and EPR spectroscopies.

4.2 THEORY

The single d-electron of the \(\text{VO}^{2+}\) ion occupies the \(t_{2g}\) orbital in the octahedral crystal field and gives rise to \(^2T_{2g}\) ground state. When excited, the electron occupies the upper \(e_g\) orbital and gives rise to \(^2E_g\) term. In ideal octahedral symmetry, only one band arising from the transition \(^2T_{2g} \rightarrow ^2E_g\) is expected. However, \(\text{VO}^{2+}\) never exhibits an ideal octahedral symmetry but lowers to tetragonal \((\text{C}_{4v})\) or still lower symmetries like \(\text{C}_{2v}\) because of the non-symmetrical alignment of the \(\text{V} = \text{O}\) bond. In \(\text{C}_{4v}\) symmetry, \(^2T_{2g}\) splits into \(^2B_2\) and \(^2E\), where as \(^2E_g\) splits into \(^2B_1\) and \(^2A_1\). Accordingly, three bands are expected due to the transitions from the
ground state ($^2B_2$) to the exited states $^2E$, $^2B_i$, and $^2A_i$). The general ordering of energy levels is as follows [27,28]

$$^2B_2 < ^2E < ^2B_i < ^2A_i$$

If the symmetry is still lowered, the degeneracy of the $^2E$ level will also be removed. For example, in the $C_{2v}$ symmetry, $^2E$ splits into $^2B_1$ and $^2B_2$. This results in four bands. The energy level diagram for d$^1$ in octahedral ($O_h$), tetragonal ($C_{4v}$) and rhombic ($C_{2v}$) symmetries is shown in Fig 4.1 and the Energy level diagram for VO$^{2+}$ ion is shown in Fig 4.2.

Fig 4.1 Correlation of different electronic states in $O_h$, $C_{4v}$ and $C_{2v}$ symmetries for d configuration
Fig 4.2 Energy level diagram for VO$^{2+}$ ion
4.3 EXPERIMENTAL

The starting materials used in the present study are analar grade Li$_2$CO$_3$ (99.9%), Na$_2$CO$_3$ (99.9%), CdO (99.9%) and P$_2$O$_5$ (99.9%). The host glass composition is taken as $x$ Li$_2$O + (20- $x$) Na$_2$O + 20 CdO + 59.5 P$_2$O$_5$ + 0.5 V$_2$O$_5$ (5 ≤ $x$ ≤ 15). Each batch is first sintered at 700 K and then melted in an electric furnace at 1250 K for nearly 2h, using Platinum crucible. The melt is then quenched at room temperature in air to form a glass. The glasses so formed are annealed at 550 K for 30 minutes. X-ray diffraction is used to ensure the amorphous nature of the glass. The measurements are performed on a PHILIPS XPERT PRO X-RAY diffraction system. EPR spectra are recorded at room temperature on JES-FA series X-band EPR spectrometer having 100 kHz field modulations. Optical absorption spectra of glasses are recorded at room temperature on JASCO (V-550) Spectrophotometer in the wavelength range 200-900 nm.
4.4 RESULTS AND DISCUSSION

Powder XRD spectra are recorded for the three VO\textsuperscript{2+} doped mixed alkali cadmium phosphate glass samples and a typical one for a glass sample is shown in Fig.4.3. The observed X-ray pattern of the samples studied in the present investigation indicates amorphous nature for the glasses. Hence, the formation of glass in these samples is confirmed.

![XRD pattern](image)

Fig 4.3 XRD pattern of Vanadyl doped Li-Na Cadmium Phosphate glass

Optical absorption spectrum of VO\textsuperscript{2+} doped mixed alkali Cadmium Phosphate glasses are shown in Fig 4.4(a,b,c). This shows three bands for each glass and this exhibits the characteristic of VO\textsuperscript{2+} ion in tetragonally distorted octahedral site and these bands are attributed to the transitions $^2\text{B}_2 \rightarrow ^2\text{E}$, $^2\text{B}_2 \rightarrow ^2\text{B}_1$, $^2\text{B}_2 \rightarrow ^2\text{A}_1$. 
Fig. 4.4a. Optical absorption spectra of VO1 glass.
Fig. 4.4b. Optical absorption spectra of VO2 glass
Fig. 4.4c. Optical absorption spectra of VO3 glass
The crystal field and tetragonal distribution parameters are evaluated by the following equations:

\[ ^2B_2 \rightarrow ^2E : -3D_s + 5D_t \quad : 12342, 12342 \text{ and } 12419 \text{ cm}^{-1} \]

\[ ^2B_2 \rightarrow ^2B_1 : 10D_q \quad : 14702, 14659 \text{ and } 14702 \text{ cm}^{-1} \]

\[ ^2B_2 \rightarrow ^2A_1 : 10D_q - 4D_s - 5D_t \quad : 27020, 27020 \text{ and } 27020 \text{ cm}^{-1} \]

The evaluated parameters are:

\[ D_q = 1470; \quad D_s = -3523; \quad D_t = 354; \quad \text{for VO1 glass}, \]
\[ D_q = 1466; \quad D_s = -3529; \quad D_t = 351; \quad \text{for VO2 glass and} \]
\[ D_q = 1470; \quad D_s = -3534; \quad D_t = 363; \quad \text{for VO3 glass respectively}. \]

The EPR spectra of the investigated samples exhibit resonance signals due to vanadyl ions entering the glass matrix as paramagnetic species VO\(^{2+}\). Fig. 4.5 shows the EPR spectra of V\(_2\)O\(_5\) molecules in x Li\(_2\)O + (20-x) Na\(_2\)O + 20 CdO + 59.5 P\(_2\)O\(_5\) + 0.5 V\(_2\)O\(_5\) (5 \leq x \leq 15) glasses as a function of x. From this, it is clear that the EPR spectra have structures, which are characteristic of a hyperfine interaction arising from an unpaired electron with a \(^{51}\)V nucleus whose nuclear spin is 7/2. However, from Fig 4.5, that the EPR spectra exhibit marked composition dependence as a function of x, even though we have doped the glasses with a constant V\(_2\)O\(_5\)
content in this series. This change might be due to the mixed alkali content, which play a significant role in accommodating the Vanadyl ions in the glass matrix. The EPR spectra of these samples showed a very similar pattern to others reported for Vanadyl ions in various glass systems [29-59].
Fig. 4.5a Polycrystalline EPR spectra of Vanadyl doped Li-Na Cadmium Phosphate VO1 glass
Fig. 4.5b Polycrystalline EPR spectra of Vanadyl doped Li-Na Cadmium Phosphate VO2 glass
Fig. 4.5c Polycrystalline EPR spectra of Vanadyl doped Li-Na Cadmium Phosphate VO3 glass
The EPR spectra for VO$^{2+}$ ions in glasses could be best analyzed by using an axial spin-Hamiltonian [60].

$$H = g_0 \beta B_z S_z + g_\perp \beta (B_x S_x + B_y S_y) + A_0 S_z I_z + A_\perp (S_x I_x + S_y I_y)$$

where $\beta$ is the Bohr magneton; $g_0$ and $g_\perp$ are the parallel and perpendicular principal components of the $g$ tensor; $A_0$ and $A_\perp$ are the parallel and perpendicular principal components of the hyperfine coupling tensors; $B_x$, $B_y$ 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 the spin operators of the electron and nucleus, respectively. The solutions of the spin-Hamiltonian for the parallel and perpendicular hyperfine lines are

$$B_0(m) = B_0(0) - A_0(m) - \left( \frac{64}{3} - m^2 \right) \frac{A_\perp^2}{2B_0(0)}$$

$$B_\perp(m) = B_\perp(0) - A_\perp(m) - \left( \frac{64}{3} - m^2 \right) \frac{A_0^2 + A_\perp^2}{4B_\perp(0)}$$

where $m$ is the magnetic quantum number of the Vanadium nucleus, which takes the values $\pm 7/2, \pm 5/2, \pm 3/2$ and $\pm 1/2$.

$$B_0(0) = \frac{h \nu}{g_0 \beta} \quad \text{and} \quad B_\perp(0) = \frac{h \nu}{g_\perp \beta}$$

The spin-Hamiltonian parameters are usually determined by using above equations and the calculated values are

$g_0 = 1.9254$, $g_\perp = 1.9772$, $A_0 = 183 \times 10^4 \text{ cm}^{-1}$, $A_\perp = 61 \times 10^4 \text{ cm}^{-1}$ for VO1 glass.


\[ g_\parallel = 1.9283, \quad g_\perp = 1.9772, \quad A_\parallel = 185 \times 10^4 \text{ cm}^{-1}, \quad A_\perp = 61 \times 10^4 \text{ cm}^{-1} \text{ for VO}_2 \text{ glass and} \]

\[ g_\parallel = 1.9237, \quad g_\perp = 1.9785, \quad A_\parallel = 185 \times 10^4 \text{ cm}^{-1}, \quad A_\perp = 62 \times 10^4 \text{ cm}^{-1} \text{ for VO}_3 \text{ glass respectively}. \]

An octahedral site with a tetragonal compression would give \( g_\parallel < g_\perp < g_e \) and \( |A_\parallel| > |A_\perp| \) \([41,42]\). It is observed that the spin-Hamiltonian parameters \((g \text{ and } A)\) do not vary much with the change in composition in this series of mixed alkali borate glasses. The \( g \) and \( A \) values obtained in the present work agree with the relationship \( g_\parallel < g_\perp < g_e \) and \( |A_\parallel| > |A_\perp| \) and are close to those vanadyl complexes as reported by other systems \([29-59]\). These evaluated parameters are in tune with the some other reported glass systems given in Table 4.1. It is therefore confirmed that the vanadyl ions in the present glasses exist as \( \text{VO}^{2+} \) ions in octahedral coordination with a tetragonal compression and have \( C_{4v} \) symmetry. The bonding of the vanadyl ion in ligand field of octahedral symmetry has been well characterized by earlier workers \([41,44,45]\). The \( \text{V}^{4+} \) site in the \( \text{VO}^{2+} \) ion forms coplanar bonds with each of the four oxygen ligands. The vanadyl oxygen is attached axially above the \( \text{V}^{4+} \) site along the \( Z \)-axis while the sixth oxygen forming the octahedral \( \text{O}^{}-\text{V}^{4+}-\text{O} \) unit lies axially below the \( \text{V}^{4+} \) site. The vanadyl ion (\( \text{VO}^{2+} \)) is known to form an octahedral oxygen
complex and V=O direction will be predominant axial distortion. It clearly shows that the vanadyl oxygen forms the apex V-O bond [62].

The dipolar coupling constant (P) and Fermi-constant coupling parameter (K) are evaluated using the following formulae [28].

$$A_\parallel = P \left[ (-4/7) - K + (g_\parallel - g_e) + (3/7) (g_\perp - g_e) \right]$$

$$A_\perp = P \left[ (2/7) - K + (11/14) (g_\parallel - g_e) \right]$$

where $g_e = 2.0023$. The values evaluated are

- $K = 0.73$ ; $P = -132 \times 10^{-4}$ for VO1 glass
- $K = 0.72$ ; $P = -134 \times 10^{-4}$ for VO2 glass and
- $K = 0.73$ ; $P = -133 \times 10^{-4}$ for VO3 glass respectively.

The molecular orbital co-efficients $\beta^*^2$, $\varepsilon_x^*^2$ are evaluated by the optical and EPR data using the formulae[28].

$$\beta^*^2 = \frac{(g_e - g_\parallel)A_\perp}{2\lambda} ; \quad \varepsilon_x^*^2 = \frac{(g_e - g_\perp)A_\perp}{2\lambda} ;$$

here the free ion value of spin orbit coupling constant for VO$^{2+}$ is $\lambda = 170$ cm$^{-1}$. $\Delta_\parallel$ and $\Delta_\perp$ are the energies of the electronic transitions $^2B_2 \rightarrow ^2B_1$ and $^2B_2 \rightarrow ^2E$ respectively. The evaluated values are $\beta^*^2 = 0.83, 0.80, 0.85$ ; and $\varepsilon_x^*^2 = 0.91, 0.91, 0.87$; for VO1 glass, VO2 glass and VO3 glass respectively.
Table 4.1
Comparison of spin-Hamiltonian parameters for VO\(^{2+}\) ion different systems

<table>
<thead>
<tr>
<th>System</th>
<th>(g_{ll})</th>
<th>(g_{in})</th>
<th>(A_{ll})</th>
<th>(A_{in})</th>
<th>Ref.</th>
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<tr>
<td>Na(_2)O-Si(_4)O(_2)</td>
<td>1.938</td>
<td>1.993</td>
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<td>62</td>
<td>[63]</td>
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<td>K(_2)O-Si(_4)O(_2)</td>
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<td>62</td>
<td>[63]</td>
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<td>Cs(_2)O-Si(_4)O(_2)</td>
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<td>1.995</td>
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<td>[63]</td>
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<tr>
<td>Na(_2)O-B(_2)O(_3)</td>
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<td>1.980</td>
<td>168</td>
<td>61</td>
<td>[64]</td>
</tr>
<tr>
<td>Li(_2)O-B(_2)O(_3)</td>
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<td>1.987</td>
<td>174</td>
<td>64</td>
<td>[65]</td>
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<td>Na(_2)O-B(_2)O(_3)</td>
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<td>175</td>
<td>63</td>
<td>[65]</td>
</tr>
<tr>
<td>K(_2)O-B(_2)O(_3)</td>
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<td>1.987</td>
<td>174</td>
<td>62</td>
<td>[65]</td>
</tr>
<tr>
<td>Cs(_2)O-B(_2)O(_3)</td>
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<td>1.988</td>
<td>173</td>
<td>62</td>
<td>[65]</td>
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<td>ZnO-B(_2)O(_3)</td>
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<td>[66]</td>
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<td>PbO-B(_2)O(_3)</td>
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<td>1.960</td>
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<td>57</td>
<td>[66]</td>
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<td>1.975</td>
<td>171</td>
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<td>[67]</td>
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<td>Li(_2)O-BaO-B(_2)O(_3)</td>
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<td>167</td>
<td>59</td>
<td>[68]</td>
</tr>
<tr>
<td>Li(_2)O-CaO-B(_2)O(_3)</td>
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<td>1.972</td>
<td>169</td>
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<td>[68]</td>
</tr>
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<td>1.970</td>
<td>167</td>
<td>61</td>
<td>[68]</td>
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<tr>
<td>Li(_2)O-Na(_2)O-B(_2)O(_3)</td>
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<td>1.956</td>
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<td>51</td>
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<td>CoO-BaO-B(_2)O(_3)</td>
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<td>1.958</td>
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<td>55</td>
<td>[70]</td>
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<tr>
<td>Li(_2)SO(_4)-CdSO(_4)-B(_2)O(_3)</td>
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<td>1.989</td>
<td>187</td>
<td>66</td>
<td>[71]</td>
</tr>
<tr>
<td>Na(_2)SO(_4)-CdSO(_4)-B(_2)O(_3)</td>
<td>1.928</td>
<td>1.989</td>
<td>187</td>
<td>67</td>
<td>[71]</td>
</tr>
<tr>
<td>K(_2)SO(_4)-CdSO(_4)-B(_2)O(_3)</td>
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<td>1.988</td>
<td>188</td>
<td>67</td>
<td>[71]</td>
</tr>
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<td>ZnO-P(_2)O(_5)</td>
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<td>1.982</td>
<td>157</td>
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<td>[72]</td>
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<td>Na(_2)O-P(_2)O(_5)</td>
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<td>1.979</td>
<td>175</td>
<td>59</td>
<td>[73]</td>
</tr>
<tr>
<td>Li(_2)O-Na(_2)O-CdO-P(_2)O(_5)</td>
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<td>1.977</td>
<td>183</td>
<td>61</td>
<td>Present work</td>
</tr>
<tr>
<td>Li(_2)O-Na(_2)O-CdO-P(_2)O(_5)</td>
<td>1.928</td>
<td>1.977</td>
<td>185</td>
<td>61</td>
<td>Present work</td>
</tr>
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<td>Li(_2)O-Na(_2)O-CdO-P(_2)O(_5)</td>
<td>1.924</td>
<td>1.978</td>
<td>185</td>
<td>62</td>
<td>Present work</td>
</tr>
</tbody>
</table>
4.5 CONCLUSIONS:

The results and discussion indicate a tetragonally distorted octahedral site for \( \text{VO}^{2+} \) ions in these glasses. In the vanadium doped glasses, if \( \text{V}^{4+} \) is the dopent, the distortion must be tetragonally elongated octahedron. However, the EPR studies show that \( g_{\perp} > g_{||} \) indicating tetragonally compressed octahedral site for the ion. Thus, it is to be inferred that vanadium enters the glasses as \( \text{VO}^{2+} \) ion.

The values of \( (g_{\perp} - g_{||}) \) are 0.0518, 0.0489 and 0.0548 for \( \text{VO}1 \) glass, \( \text{VO}2 \) glass and \( \text{VO}3 \) glass respectively. It indicates the tetragonal distortion is more in \( \text{VO}3 \) glass. The optical absorption spectra also suggest the same. For \( \text{VO}2 \) glass the tetragonal distortion is less when compared to other two glasses due to mixed alkali effect.

The low values of \( \kappa \) indicates the poor contribution of the vanadium 4s orbital to the vanadyl bond in these glasses. The site symmetry is \( C_{4v} \).

The covalance degree of the in-plane \( \text{V-O} \sigma \) bonds (\( \beta^{*2} \)) and \( \pi \)-bonding with the vanadyl oxygen (\( \epsilon_{\pi}^{*2} \)) in all these glasses indicates partially covalent.
REFERENCES:


