AN ESR AND OPTICAL STUDY OF VANADIUM DOPED K₂O - CdO - B₂O₃ – SiO₂

(KCdBSi) GLASSES

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ABSTRACT

Glasses of the 20K₂O - 5CdO - 60B₂O₃ -15SiO₂ and (20-x) K₂O - 5CdO - 60B₂O₃ - 15SiO₂ – xV₂O₅ (where x=0.1to 0.5mol %) KCdBSi systems were prepared by melt quenching technique. Optical and structural properties of undoped glass, and glasses doped with VO²⁺ ions were examined. Their structural properties were determined with XRD, Fourier Transform Infrared (FTIR) and Electron Paramagnetic Resonance spectra (ESR) and Optical absorption spectra. Optical band gaps of glass samples were determined for direct and indirect transitions from the absorption spectra. Through the fundamental Ultra Violet absorption edges of the glasses, the Optical band gap energies and Urbach energies were evaluated. The ESR spectra of all the glass samples exhibit resonance signals characteristic of VO²⁺ ions. The values of Spin-Hamiltonian parameters indicated that the VO²⁺ ion in KCdBSi glasses were present in octahedral sites with tetrahedral compression and belong to C₄ᵥ symmetry. Spin Hamiltonian parameters ‘g’ and ‘A’ were calculated from their Ultra Violet edges.

KEYWORDS: Borosilicate, Vanadium, Optical Absorption, Electron Spin Resonance (ESR)

INTRODUCTION

In recent years there has been a considerable interest in the study of glasses doped with transition metal ions because of their technological applications. Borosilicate glasses constitute a subject of wide spread of interest in number of fields from the earth science to glass industry in particular for special glasses i.e., Pyrex, or optical glasses and also for storage of Nuclear waste. The early research was of great importance because it was the first attempt to study symmetrically the relationships between the composition of glass and its physical and chemical properties [1]. In the next century the studies of borosilicate glass will become more and more, the applications are wide and wider. Borosilicate glasses were widely used in optical glasses, heat resistant glasses and electronic glass industry for its excellent properties [2]. Semi conducting transition metal oxide such as V₂O₅ based glasses have gained much interest in solid state chemistry and materials science with regard to their possible applications as memory and switching devices [3]. On the other hand potassium Borosilicate glasses have been widely used in the ceramic industry for the fabrication of glaze glass coatings intended for the application on faience porcelain and other types of ceramics [4]. Vanadium belongs to the unfilled 3d elements and possesses many valence states. The V²⁺, V³⁺, V⁴⁺ and V⁵⁺ states are the most well-known valence sates of vanadium in oxide glasses. Vanadate glasses are identified as n-type semiconductors for low V⁴⁺/V⁵⁺ ratio [6]. It is also known that V⁵⁺ in low ratios enter the amorphous structure as an impurity whereas V⁵⁺ in high ratios are present in the structure as glass

\[ V^{4+} \rightarrow O \rightarrow V^{5+} \Leftrightarrow V^{5+} \rightarrow O \rightarrow V^{4+} \]

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formers [7]. Some authors studied the effect of single [8] and multiple [9] TM (transition metal) ions as dopant in alkali and alkaline earth oxide glasses [10]. Binary and ternary $V_2O_5$ glasses can exhibit a semiconducting behaviour which arises from an unpaired 3d\(^1\) electron hopping between the transition metal(TM) ions when the TM ions exist in two or more valence states, i.e., an electron hopping from a $V^2$ site to a $V^3$ [11]. Glasses doped with TM ions came into prominence because of their notable spectroscopic properties and their suitability for fiber optic communications, luminescent solar energy concentrators (LSCs) [12]. In the present study, the absorption and transmission of $20K_2O - 5CdO - 60B_2O_3 - 15SiO_2$ and $(20-x) K_2O - 5CdO - 60B_2O_3 - 15SiO_2 - xV_2O_5$ (where $x=0.1$ to $0.5\text{mol\%}$) glasses (KCdBSi systems), Optical band gaps and Urbach energies were calculated. Defects of the surfaces and their spectroscopic properties were determined by Optical and ESR studies.

**EXPERIMENTAL**

Glass samples were prepared in the composition $(20-x) K_2O - 5CdO - 60B_2O_3 - 15SiO_2 - xV_2O_5$ for Vanadium doped samples where $x = 0, 0.1$ to $0.5\text{mol\%}$ $V_2O_5$. Using digital balance of sensitivity $\pm 0.0001\text{gms}$, appropriate amount of chemicals in powder form were weighed and grounded into fine powder and mixed thoroughly. The samples were melted in silica crucibles in an electrical furnace at temperature range of $1100^\circ\text{C}-1200^\circ\text{C}$ for 10 minutes. The melted samples were poured on a clean polished brass plate and carefully pressed with another brass plate to get uniform thickness of the glass. The glasses obtained are transparent and were light greenish in colour. The obtained glasses were polished finely to obtain optical measurements. Optical absorption spectra were recorded at room temperature on JASCO V-670 Spectrophotometer with 200-900 nm. ESR readings were made at room temp on JEOL-JM FE3 with 100 KHz field modulation ESR spectrometer.

**RESULTS AND DISCUSSIONS**

**Optical Absorption Spectra**

The study of optical absorption and particularly the absorption edge is a useful method for the investigation of optically induced transitions and for the provision of information about the band structure and energy gap in both crystalline and non-crystalline materials.

The principle of this technique is that a photon with energy greater than the band gap energy will be absorbed. Two types of optical transitions, i.e., direct and indirect, occur at the absorption edge[13-15]. The absorption as a function of wavelength for all compositions of glass is shown in Figure 1.

![Figure 1: Optical Absorption Band Spectrum of VO\(^{2+}\) Ion Doped in KCdBSi Glass Systems](image-url)

The absorption coefficient, below and near the edge of each curve was determined at different wavelengths using relation (1).
An ESR and Optical Study of Vanadium Doped K₂O - CdO - B₂O₃ – SiO₂ (KCdBSi) Glasses

\[ \alpha(\omega) = B e^{\frac{1}{\omega \Delta E}} \]  

(1)

where \( \alpha(\omega) \) is the absorption coefficient at an angular frequency of \( \omega = 2\pi \nu \), \( B \) is the band tailoring parameter and \( \Delta E \) is the width of the tail of localized states in the band gap (Urbach energy). At the absorption edge, random internal electric fields will dominate the broadening of the excitation levels due to the lack of long-range order or presence of defects [16]. The two kinds of optical transitions at the fundamental edge of crystalline and non-crystalline semiconductors—direct transitions and indirect transitions, both of which involve the interaction of an electromagnetic wave with an electron in the valence band, which is then raised across the fundamental gap to the conduction band. For the direct optical transition from the valence band to the conduction band it is essential that the wave vector for the electron be unchanged. In the case of indirect transitions the interaction with the lattice vibrations (phonons) takes place. Thus the wave vector of the electron can change in the optical transition and the momentum change will be taken or given up by phonons. Hence, the absorption coefficient \( \alpha(\nu) \) can be determined near the edge using the formula:

\[ \alpha(\nu) = \frac{1}{d} \ln \left( \frac{I_0}{I} \right) = 2.303 \left( \frac{A}{d} \right) \]  

(2)

where \( A \) is the absorbance at frequency \( \nu \) and \( d \) is the thickness of the sample.

The absorbance coefficient \( \alpha(\nu) \) as a function of the photon energy (hv) for direct and indirect optical transitions according to Mott and Davis [17] is given by

\[ \alpha(\nu) = B (hv - E_{op})^n / hv \]  

(3)

where \( B \) is an energy-independent constant band tailoring or band edge steepness parameter in Tauc’s picture [18] and the index ‘n’ takes different values depending on the mechanism of inter band transitions i.e., \( n = 2 \) and \( 1/2 \) for direct allowed transitions and indirect allowed transitions respectively. For most of the amorphous materials indirect transitions are favoured according to Tauc’s [18] Picture.

Figure 2: Direct Bands of VO²⁺ Ion Doped in KCdBSi Glass Systems

Figure 3: Indirect Bands of VO²⁺ Ion Doped in KCdBSi Glass Systems
The values of indirect optical band gap energy $E_{opt}$ can be obtained from Eq.(4) by extrapolating the absorption coefficient to zero absorption in $(\alpha h\nu)^{1/2}$ vs $h\nu$ plot and is shown in Figure 3. Plots were also drawn between $\ln\alpha$ and $h\nu$ shown in Figure 4 and from these plots the slopes and thereby Urbach energies have been calculated. Figure 1, represents the Optical absorption spectra of present work KCdBSi glasses recorded at room temperature in the wavelength region 200-1400nm. The spectrum of glasses $V_1$ exhibited two broad absorption bands at 456 nm and 627 nm corresponds to $^2B_{2g} \rightarrow ^2B_{1g}$ and $^2B_{2g} \rightarrow ^2E_g$ transitions of $VO^{2+}$ ions. With the increase of concentration of $V_2O_5$, the half width and peak height of these bands are found to increase up to 0.5% of $V_2O_5$ and thereafter the intensity of the bands is found to decrease. Figures 2, 3 and 4 represents the direct, indirect and Urbach plots of all these glasses in which a considerable part of each curve is observed to be linear. The values of optical band gap ($E_{opt}$) for direct, indirect, and Urbach plots obtained from the extrapolation of these curves are present in Table 1.

Table 1: Summary of the Data on Optical Absorption Spectra and Direct, Indirect, Urbach Energy of $VO^{2+}$ Ion Doped KCdBSi Glass Systems

<table>
<thead>
<tr>
<th>Glass Sample</th>
<th>Cut off Wave Length (nm)</th>
<th>$^2B_{2g} \rightarrow ^2B_{1g}$ (nm)</th>
<th>$^2B_{2g} \rightarrow ^2E_g$ (nm)</th>
<th>Direct (Eopt) eV</th>
<th>Indirect (Eopt) eV</th>
<th>Urbach Energy ($\Delta E$) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>V1</td>
<td>321</td>
<td>456</td>
<td>627</td>
<td>3.328</td>
<td>3.864</td>
<td>3.756</td>
</tr>
<tr>
<td>V2</td>
<td>330</td>
<td>431</td>
<td>605</td>
<td>3.320</td>
<td>3.640</td>
<td>3.653</td>
</tr>
<tr>
<td>V3</td>
<td>342</td>
<td>450</td>
<td>607</td>
<td>3.155</td>
<td>3.558</td>
<td>3.564</td>
</tr>
<tr>
<td>V4</td>
<td>348</td>
<td>430</td>
<td>604</td>
<td>2.904</td>
<td>3.508</td>
<td>3.521</td>
</tr>
<tr>
<td>V5</td>
<td>349</td>
<td>458</td>
<td>633</td>
<td>2.455</td>
<td>3.472</td>
<td>3.456</td>
</tr>
</tbody>
</table>

ESR Study

No ESR signal is observed in undoped glasses confirming that the starting material used in the present work is free from transition metal impurities or other paramagnetic centers (defects). The ESR spectra of all the investigated samples from $V_1$ to $V_5$ exhibit resonance signals and are shown in Figure 5.

Because of the low content of $V_2O_5$ (i.e., x=0.1 to 0.5 mol %) these spectra shows a well-resolved hyperfine structure (hfs) typical for vanadyl ions in a $C_{4v}$ symmetry. The 16 - line feature with eight parallel and eight perpendicular lines is typical of the unpaired (3d$^1$) electron of VO$^+$ ion in association with $^{51}V$ ( I=7/2 ) in an axially symmetric crystal field [19].
An ESR and Optical Study of Vanadium Doped K₂O - CdO - B₂O₃ – SiO₂ (KCdBSi) Glasses

The analysis of well resolved hyperfine structure of the ESR spectra was made using an axial spin-Hamiltonian.

\[ H = g \parallel B S_x + g \perp B (S_x S_y + S_y S_z) + A \parallel S_z I_z + A \perp (S_x I_x + S_y I_y) \]  \hspace{1cm} (5)

where \( \beta \)-Bohr magneton. \( g \parallel \) and \( g \perp \) are the parallel and perpendicular principle components of \( g \) tensor. \( B_x, B_y, B_z \) – components of the magnetic field. \( S_x, S_y, S_z, I_x, I_y, I_z \) – components of the electron and nucleus spin operator. \( A \parallel \) and \( A \perp \) are principle components of the hyperfine coupling tensor. The values of the magnetic field for the hyperfine peaks from the parallel and perpendicular absorption [20] bands are given by

\[ B \parallel (m_l) = B \parallel (0) - A \parallel (m_l) - (63/4 - m_l^2) A \perp^2 / 2 B \parallel (0) \]  \hspace{1cm} (6)

\[ B \perp (m_l) = B \perp (0) - A \perp (m_l) - (63/4 - m_l^2) (A \parallel^2 - A \perp^2) / 4B \perp (0) \]  \hspace{1cm} (7)

where \( m_l \) is the magnetic quantum number of the vanadium nucleus, which takes the values \( \pm 7/2, \pm 5/2, \pm 3/2, \pm 1/2 \).

\[ B \parallel (0) = h \nu / g \parallel \beta \] \text{ and } \[ B \perp (0) = h \nu / g \perp \beta \]

where the symbols have their usual meaning and \( \nu \) is the microwave frequency. ESR parameters of studied glasses are given in Table 2. The values obtained are in good agreement with the other reports given in literature [19,21-23]. The data shows that \( g \parallel < g \perp < g_e \) and \( A \parallel > A \perp \). The relation that corresponds to vanadyl ions in KCdBSi glasses exist as VO\(^{2+}\) ions in octahedral coordination with a tetragonal compression and have a \( \text{C}_4\text{v} \) symmetry. The vanadyl oxygen is attached axially above the \( \text{V}^{4+} \) site along the \( Z \)-axis (\( \text{V}=\text{O} \) bond) while the sixth oxygen forming the \( \text{O}-\text{VO}_{4}-\text{O} \) unit lies axially below the \( \text{V}^{4+} \) site in opposition with “yl” Oxygen. The predominant axial distortion of the VO\(^{2+}\) octahedral oxygen complex along \( \text{V}=\text{O} \) direction may be the reason for very less variation of \( g \) and \( A \) values for all the glass samples [21]. Fermi contact interaction term (\( K \)) and dipolar hyperfine coupling parameter (\( P \)) are evaluated using the expressions developed by Kivelson and Lee [24].

\[ A \parallel = -P \{ (K-4/7) \cdot A g \parallel - 3/7 \cdot A g \perp \} \]  \hspace{1cm} (8)

\[ A \perp = -P \{ (K-2/7) - 11 / 14 A g \perp \} \]  \hspace{1cm} (9)

where \( A g \parallel = g \parallel - g_e \) , \( A g \perp = g \perp - g_e \) and \( g_e = 2.0023 \) is the \( g \) factor of the free electrons [25]. The values of \( (A g \parallel / \Delta g \perp) \) which measure the tetragonality of the \( \text{V}^{4+} \) site are also calculated and are presented in Table 4. A decrease in \( (A g \parallel / \Delta g \perp) \) shows that the octahedral symmetry around \( \text{V}^{4+} \) ions is improved [30]. From data \( V_1 \) sample value of \( A \parallel \) and \( P \) is very high compared to other samples.
Table 2: Summary of the Spin Hamiltonian Parameters, Molecular Orbital Coefficients of VO\textsuperscript{2+} Ion Doped KCdBSi Glasses

| Glass Sample | g\textsubscript{||} | g\textsubscript{⊥} | A\textsubscript{||} 10\textsuperscript{-4} cm\textsuperscript{-1} | A\textsubscript{⊥} 10\textsuperscript{-4} cm\textsuperscript{-1} | \(\Delta g\textsubscript{||} / \Delta g\textsubscript{⊥}\) | k | P |
|--------------|----------------|----------------|-------------------------------|-------------------------------|--------------------------------|---|---|
| pure         | -              | -              | -                             | -                             | -                             | - | - |
| V\textsubscript{1} | 1.948          | 1.992          | 241.9                         | 72.6                          | 5.71                          | 0.637 | -210 |
| V\textsubscript{2} | 1.972          | 1.999          | 197.2                         | 58.2                          | 11.1                          | 0.633 | -168 |
| V\textsubscript{3} | 1.994          | 1.976          | 172.0                         | 66                            | 0.3                           | 0.83  | -123 |
| V\textsubscript{4} | 1.991          | 1.987          | 182.0                         | 72                            | 0.67                          | 0.85  | -129 |
| V\textsubscript{5} | 1.931          | 1.969          | 175.9                         | 52.9                          | 2.02                          | 0.66  | -152 |

CONCLUSIONS

- The Optical band gap energy varies from 2.455 eV to 3.328 eV for direct 3.472 eV to 3.56 eV for Urbach plots. It shows linear increment and decrement in energy values. The physical parameter density results showed that the introduction of V\textsubscript{2}O\textsubscript{5} into a KCdBSi glasses shows a small increase.

- The optical Absorption study indicate the presence of Vanadium predominantly in VO\textsuperscript{2+} state which takes modifier positions, if V\textsubscript{2}O\textsubscript{5} is present in lower Concentrations (up to 0.5mol %).

- The ESR and Optical absorption spectra of V\textsubscript{2}O\textsubscript{5} doped in KCdBSi glasses have been successfully interpreted as the presence of six coordinate tetravalent Vanadium existing as a vanadyl complex with a tetragonally compressed octahedral site.

- The spin Hamiltonian parameters g and A are found to be independent of V\textsubscript{2}O\textsubscript{5} content. The increase in \(\Delta g\textsubscript{||} / \Delta g\textsubscript{⊥}\) value indicates the improved octahedral symmetry around VO\textsuperscript{2+} ion.

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