EPR and Optical absorption of Vanadyl ions in CdO-ZnO-LiF- B_2O_3-P_2O_5 Glasses

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Abstract

Electron paramagnetic resonance (EPR) and optical absorption spectra of Vanadyl ions in CdO-ZnO-LiF-B_2O_3-P_2O_5 Glasses have been studied. The spin-Hamiltonian parameters (g and A), Fermi contact interaction parameter (k) and crystal field parameters have been evaluated. The values of spin-Hamiltonian parameters confirm the presence of VO^{2+} ions in an octahedral site with a tetragonal compression. The optical properties of present glass system are studied from the optical absorption spectra recorded in the wavelength range 200-1100 nm. The optical band gap for direct and indirect allowed transitions and Urbach energies have been determined. The details were presented in the paper.

Key words: EPR, Optical absorption spectra, CdO-ZnO-LiF-B_2O_3-P_2O_5 Glasses.

1. Introduction

The inorganic glasses containing transition metal ions have attracted the scientific community because their technological importance in electronics, tunable solid state lasers and fiber optic communication systems. Transition metal ions can be used as probe to study the glass structure because their sensitive responses to the surrounding cations.. Also the study of transition metal ions in amorphous matrix is one of the interesting research subjects both from the theoretical and experimental points of view [1-3].

A number of papers have been published on alkali-fluoroborate glasses, for example Shelby and Ortolano prepared NaF-Na_2O-B_2O_3 glass system and studied the refractive index, density and glass transition temperature. Marimuthu et al. studied the structural and optical properties of alkali-fluroborate glass system B2O3-XCO_3-NaF-Eu_2O_3 (X=Li, Na, Ca and Mg). El-Hofy and Hager et.al prepared B_2O_3-BaF-LiX (X=F, Cl, Br) glasses and investigated IR and elastic moduli of the obtained glasses. Sumalatha et.al studied the EPR and optical absorption spectra of alkaline earth zinc borate glasses and found that the vanadyl ions are in +4 oxidation state [4-7].

The addition of transition metal (TM) oxides to the glasses, in general, permits the possibility for the glasses to exihibit the semiconducting behavior. Among the transition metal oxides, V_2O_5 is of much interest in the contemporary and emerging technology, wherein it finds applications in the fields like micro electronics, solid state ionics etc. [8-10].

In the present study, the EPR spectra of CdO-ZnO-LiF-B_2O_3-P_2O_5 glasses containing vanadium were studied in order to evaluate on the spin-Hamiltonian parameters and to study the optical properties of these glasses.

2. Experimental

AR grade chemicals from SD chemicals were used to prepare the glass samples of composition $10CdO\text{-}(20\text{-}x)ZnO\text{-}x\text{-}LiF\text{-}40B_2O_3\text{-}30P_2O_5$ using Cadmium carbonate, Zinc carbonate, Lithium fluoride Boric acid and Phosphoric acid. All chemicals were taken according to the molecular weight. Phosphoric acid was added to the mixture of all others at the end. 1 mol% of V_2O_5 was added as a dopant. The total batch weight was 20 gms. The grounded was melted in a porcelain crucible at $1050^{o}C$ for one hour and the melt was quenched onto stainless steel plate at $100^{o}C$. These glasses were then immediately transferred to another furnace kept at $300°C$ and annealed for 5 hours to remove thermal strains and then cooled to room temperature. The prepared glasses and their glass codes are given below.

| S.No.	Chemical Composition	Glass Code
1.	$10CdO\text{-}18ZnO\text{-}2LiF\text{-}40B_2O_3\text{-}30P_2O_5$	CZLBP-1
2.	$10CdO\text{-} 16ZnO\text{-}4LiF\text{-}40B_2O_3\text{-}30P_2O_5$	CZLBP-2
3.	$10CdO\text{-}14ZnO\text{-}6LiF\text{-}40B_2O_3\text{-}30P_2O_5$	CZLBP-3

The EPR spectra were recorded at room temperature on Brucker EPR spectrometer operating in X-band frequency (9.153GHz) with a field modulation frequency of 100 Hz. The optical absorption spectra of these glasses were recorded in the UV region to measure the optical absorption edges by using a Shimadzu spectrophotometer in the wave length range 200-1100 nm at room temperature.

3. Results and Discussion

3.1. EPR studies

Fig. 1 shows the EPR spectra of 1 mole % of V_2O_5 ions of $10CdO$-$(20$-$x)ZnO$-x-LiF-$40B_2O_3$-$30P_2O_5$ glasses. The 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 and which is present in 99.76% abundance. These spectra were analyzed by assuming that vanadium is present as vanadyl ion in ligand field of C_{4v} symmetry [11-13].

Fig. 1 EPR Spectra of 1 mole% of vanadyl ions in $10CdO$-$(20$-$x)ZnO$-x-LiF-$40B_2O_3$-$30P_2O_5$ gl**asses at room**
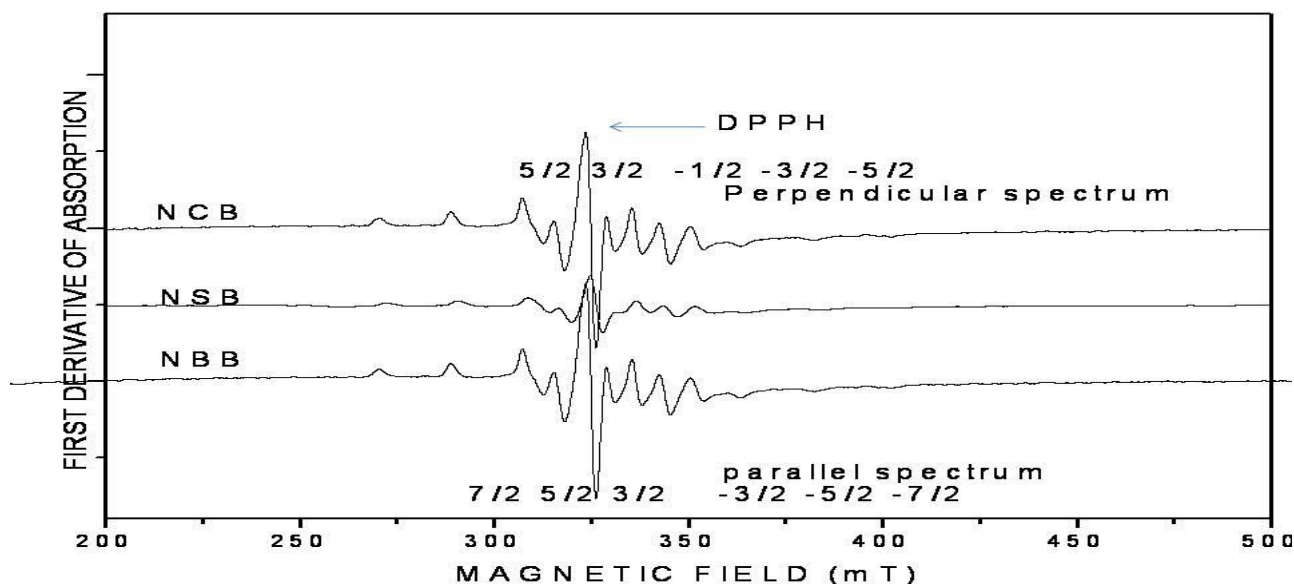
temperature

The EPR spectra of VO^{2+} ions could be analyzed by using a spin-Hamiltonian [14]

$$\mathcal{H} = g_{\|}\beta B_z S_z + g_\perp \beta (B_x S_x + B_y S_y) + A_{\|} S_z I_z + A_\perp (S_x I_x + S_y I_y) \tag{1}$$

where β is the Bohr magneton, $g_{\|}$ and $g_\perp$ are the parallel and perpendicular principal components of the g tensor, $A_{\|}$ and $A_\perp$ are the parallel and perpendicular principal components of the hyperfine coupling tensor, B_x, B_y and B_z are the components of the magnetic field, 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 given by

$$B_{\|}(m_I) = B_{\|}(0) - A_{\|}m_I - (63/4 - m_I^2)\frac{A_\perp^2}{2B_{\|}(0)} \tag{2}$$

$$B_\perp(m_I) = B_\perp(0) - A_\perp m_I - (63/4 - m_I^2) \frac{(A_\parallel^2 + A_\perp^2)}{4B_\perp(0)}$$

(3)

where m_I is the magnetic nuclear quantum number of the vanadium nucleus, which takes the values $\pm 7/2$, $\pm 5/2$, $\pm 3/2$ and $\pm 1/2$;

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

where ν is the microwave frequency.

The spin-Hamiltonian parameters are usually determined by using eqns. (2) and (3). The iterative method for the numerical analysis of the spectrum as suggested by Muncaster and Parke was used here to avoid the errors caused by certain amount of overlapping between hyperfine lines. Table 1 presents the spin-Hamiltonian parameters evaluated for different alkali fluoroborate glasses. The paramagnetism of the vanadyl ion (V^{4+}) arises from a single unpaired electron, as the crystalline fields quench the orbital angular momentum. The crystal fields of V^{4+} ions in glasses can be described either by threefold or fourfold symmetries [15]. The variation of $g_\parallel$ and $g_\perp$ depend critically on the local symmetry of this field. Although the V^{4+} ion is present usually in six-fold coordination, its local symmetry is generally a distorted octahedron of oxygen ions in many complexes.

An octahedral site with a tetragonal compression would give $g_\parallel < g_\perp < g_e$ and $A_\parallel > A_\perp$ [14, 16]. The g and A values obtained in the present work agree with this relationship and are close to those of other vanadyl complexes reported in the literature [17-21]. It is, therefore, confirmed that the vanadyl ions in the present alkali fluoroborate glasses exist as VO^{2+} ions in octahedral coordination with a tetragonal compression and have a C_{4v} symmetry.

Table 1 Spin-Hamiltonian parameters of VO^{2+} ions

Glass	$g_\parallel$	$g_\perp$	$\Delta g_\parallel$	$\Delta g_\perp$	$A_\parallel \times 10^{-4}$ (cm^{-1})	$|A_\perp| \times 10^{-4}$ (cm^{-1})
CZLBP-1	1.955	1.988	0.0462	0.0155	194	63
CZLBP-2	1.951	1.986	0.0522	0.0174	183	62
CZLBP-3	1.945	1.979	0.0553	0.0242	164	64

The value of $(\Delta g_\parallel / \Delta g_\perp)$ where $\Delta g_\parallel = (g_e - g_\parallel)$ and $\Delta g_\perp = (g_e - g_\perp)$ which measures the tetragonality of the VO^{2+} site are also calculated and are presented in Table 2. A decrease in

($\Delta g_\parallel/\Delta g_\perp$) shows that the octahedral symmetry around VO^{2+} ion is improved from CZLBP-1 to CZLBP-3 glass. It is seen from the table that($\Delta g_\parallel/\Delta g_\perp$) values decrease with alkaline earth metal ions, the deviation from octahedral symmetry decreases and the VO^{2+} ions are less tetragonally distorted [22].

Molecular orbital theory shows that the hyperfine components $A_\parallel$ and $A_\perp$ consist of the contributions of $A_\parallel'$ and $A_\perp'$ of the $3d_{xy}$ electron to the hyperfine structure and the $P\beta_2^{*2}k$ term arising due to the anomalous contribution of the s-electron.

Kivelson and Lee gave the following relations:

$$A_\parallel = A_\parallel' - P\beta_2^{*2}k \qquad\qquad (4)$$

$$A_\perp = A_\perp' - P\beta_2^{*2}k \qquad\qquad (5)$$

where

$$A_\parallel' = P[-\beta_2^{*2}(4/7) + (g_\parallel - 2.0023) + 3/7(g_\perp - 2.0023) + D_\parallel + 3/7D_\perp],$$

$$A_\perp' = P[\beta_2^{*2}(2/7) + 11/14(g_\perp - 2.0023) + 11/14D_\perp].$$

Here $P = 2\gamma\beta\beta_N\langle r^{-3}\rangle = 0.0128$ cm^{-1} is the dipolar hyperfine coupling parameter,r^{-3} is the average size of the vanadium 3d orbital and k is dimensionless Fermi contact interaction parameter, which represents the amount of unpaired electron density at the vanadium nucleus. The Fermi contact interaction term k, Pk/γ representing the s- character of the spin of vanadium and the covalency rates (1 - α ²) and (1- υ²) were calculated and are given in Table 2. The high values of k indicate a large contribution to the hyperfine constant by the s- electron. The (1 - α²) and (1- υ²) values indicated moderate covalency for σ and π-bonds respectively [23-24].

Table 2 Tetragonality and covalency rates of V⁴⁺ ions

Glass	$\Delta g_\parallel/\Delta g_\perp$	$|A'_\parallel|\times10^{-4}$ (cm^{-1})	$|A'_\perp|\times10^{-4}$ (cm^{-1})	(1 - α²)	(1- υ²)	k	Pk/γ (cm^{-1})
CZLBP-1	3.02	81	35	0.627	0.615	0.89	0.0078
CZLBP-2	3.02	80	35	0.581	0.567	0.71	0.0062
CZLBP-3	2.27	79	34	0.557	0.391	0.65	0.0057

3.2. Optical absorption studies

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.

Fig. 2 shows the optical absorption spectra of all the prepared glasses in the wavelength region of 200–800 nm and exhibit one band characteristic of V^{4+} ions in tetragonal symmetry.
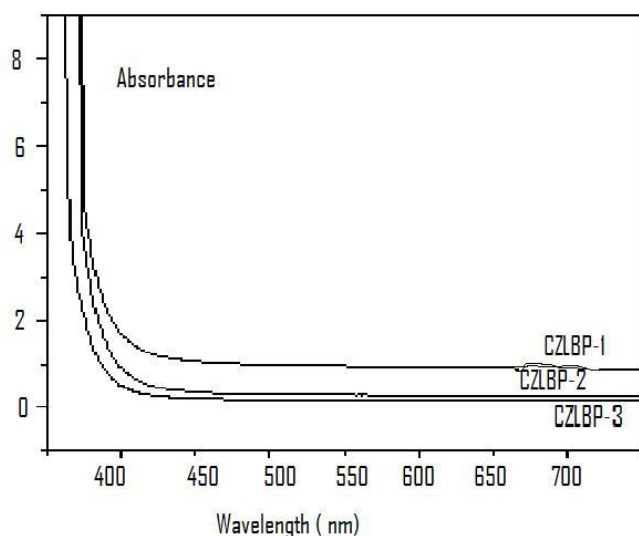
For V^{4+} ion in tetragonal symmetry, we expect three bands corresponding to the transitions $^2B_{2g} \rightarrow \,^2E_g$, $^2B_{2g} \rightarrow \,^2B_{1g}$, and $^2B_{2g} \rightarrow \,^2A_{1g}$. In the present case, for all the glass samples only the first band is observed, i.e. the band has been assigned to the transition $^2B_{2g} \rightarrow 2\,E_g$ at 376 nm, 372 nm and 369 nm wave lengths of glasses CZLBP-1, CZLBP-2 and CZLBP-3 respectively.

The absorption peak is characteristic of V^{4+} ions with a distorted octahedral site. Assignment of the absorption bands are made in the light of energy level scheme for molecular orbitals of the VO^{2+} ions in a ligand field of C_{4v} symmetry [25].

The absorption coefficient $\alpha(\upsilon)$ can be determined near the edge using the relation[26]

$$\alpha(\upsilon) = /d)\ln(I_0/I) = 2.303\,\frac{A}{d} \tag{6}$$

where the factor $\ln(I_0/I)$ is the absorbance 'A' at a frequency υ and d is the thickness of the sample. According to Davis and Mott's relation

$$\alpha(\upsilon)=B(h\upsilon - E_{opt})^n/h\upsilon \tag{7}$$

where B is an energy independent constant

n=2 is indirect allowed transition, n=3 is indirect forbidden transition

n=1/2 is direct allowed transition, n=1/3 is direct forbidden transition

According to Tauc's picture, generally indirect transitions are favored in amorphous materials [27]. In this case the value of n is 2 and eqn. (7) after rearrangement becomes

$$E_{opt} = h\upsilon - (\alpha h\upsilon / B)^{1/2} \tag{8}$$

The empirical Urbach rule is given by

$$\alpha(\upsilon) = B\exp(h\upsilon / \Delta E) \tag{9}$$

where ΔE is the Urbach energy and is found as the inverse slope of the ln (α) vs. hυ plot given in **Fig. 3** [28]. Urbach energy and the optical band gap energy (allowed direct & indirect) values are tabulated in **Table 3**.

Table 3 Optical parameters

Glass	λ_c (nm)	Urbach energy (eV)	Band gap energy (eV) indirect	direct
CZLBP-1	387	0.69	2.82	3.10
CZLBP-2	382	0.64	2.92	3.12
CZLBP-3	366	0.54	2.98	3.18

4. Conclusions

From the EPR spectra it was observed that $g_{\parallel}$ and $g_{\perp}$ values are decreasing with the change in composition of the glasses. The decrease in $g_{\parallel}$ and $g_{\perp}$ values are attributed to the increasing tetragonality at the vanadium site. The deviation from octahedral symmetry increases and the symmetry around VO^{2+} ions are more tetragonally distorted, with the change in composition The EPR and optical absorption studies show that the vanadium ions (V^{4+}) exist as VO^{2+} ions in octahedral coordination with tetragonal compression and belong to C$_{4v}$ symmetry. The optical energy gap values and the Urbach energies are found to vary linearly with atomic radii of alkaline earth metal ions.

Acknowledgements

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