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EPR and Optical Absorption studies on Vanadium doped Glasses

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Abstract : Electron Paramagnetic Resonance (EPR) and Optical Absorption studies on glasses $20Li_2O - 10\ Na_2O - (70\text{-}X)\ B_2O_3$ doped with $\mathbf{X=V_2O_5}$ are reported. EPR spectra of V^{4+} ions doped in the glass system exhibited peak at g =1.98. Spin Hamiltonian parametersg $_{\parallel}$, $g_{\perp}$,. I$A_{\parallel}$ I, I$A_{\perp}$ I, dipolar hyperfine coupling parameter P, and Fermi contact interaction parameter K, have been calculated and found that these parameters are dependent upon alkali ion concentration in the glass system and the VO^{2+} ion in an octahedral coordination with a tetragonal compression. When the concentration of V_20_5 is increased from 0.2 to 1.0 mole %, the Values of $g_{\parallel}$,P decrease; values of K increase and values of $g_{\perp}$, $A_{\parallel}$, $A_{\perp}$are found to be constant. These values show that there is a tetragonal distortion of V^{4+} in Borate Glasses. Optical absorption spectra recorded in the range 300 - 900nm at room temperature showed a band at 800 to 850nm which is attributed to $^2B_2 \rightarrow {}^2B_1and^2B_2 \rightarrow {}^2E$ transitions.

Keywords : EPR, Spin Hamiltonian Parameters, Lithium Borate Glass.

Introduction:

Electron paramagnetic resonance (EPR) spectral study on transition metal ions in glasses is an **interesting research subject**[1,2] to investigate glass structure. The ability to characterize the local structure of a paramagnetic centre and sensitive detection of structural changes form the basis for the increasing number of applications of EPR technique to glasses [3].

EPR investigations of VO^{2+} ions in glasses have received a considerable attention because the EPR parameters are very sensitive to the local symmetry. EPR spectra of VO^{2+}ions have been widely studied in a variety of glasses [4-6].The spin-Hamiltonian parameters of EPR and the bands in the optical absorption spectrum of VO^{2+}ions in glasses are sensitive to the ligands. Optical absorption is a mechanism in solids where the photon will be absorbed by either lattice or by electron. The lattice (or phonon) vibration will give information about atomic vibrations involved and this absorption of radiation usually occurs in the infrared region of spectrum. Energy gap of non-crystalline solids can be calculated from optical absorption. The principle involved in this technique is, a photon with energy greater than the band gap will be absorbed.

Experimental

The glass samples studied in the present work have been prepared by melt quenching technique. They were prepared by mixing and grinding together by appropriate amounts of Li_2O - Na_2O - B_2O_3 doped with V_2O_5 in an agate motor before transferring into crucible. The mixtures were heated in an electric furnace at 1225K for 20 min. The melt was then quenched to room temperature by pouring it on a plane brass plate and pressing it with another brass plate. Finally the vitreous sample were annealed for 3 hrs at 423K to relieve residual internal stress and slowly cooled to room temperature. White and brown coloured glasses of good optical quality and high transparency have been obtained. The polished glasses were characterized for Optical absorption and EPR.

Optical Absorption study

Optical absorption spectra of all samples were recorded on Perkin Elmer Lambda 950 with diffused reflectance spectra (DRS) accessory in the wavelength range 350–1200nm.

EPR Study

Thefirst derivative EPR spectra of the crushed specimens were recorded at room temperature in theX-band (υ = 9.3 GHz) on an EPR spectrometer (VarianE-109) using 10.0 mW microwave power. A magnetic field modulation of 100 kHz with a peak to peak (p-p) amplitude of 0.1 mT was applied. Polycrystalline DPPH was used as a standard g marker (g = 2.0036 + 0.0002).

Results and Analysis

Optical Absorption

Figure 1 shows the optical absorption spectra of$20Li_2O$– 10 Na_2O – (70-X)B_2O_3glasses doped with X=V_2O_5 . The observed absorption peaks at ~ 600 nm and 860 nm can be attributed to $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2E$ transitions, respectively(Table 1). The absorption edge observed at 400nm for the glass sample is found to be shifted slightly towards higher wavelength with increase in the concentration of V_2O_5. Additionally, the spectra of all the samples exhibited an absorption band in the region 550-650nm.There is a noticeable increase in the intensity of the spectrum in the region 800-1000nm wavelength with increase in the concentration of V_2O_5.

The largest intensity and the half width of these bands have been observed in the spectrum of glass, indicating the presence of the largest concentration ofVO^{2+} (vanadyl) ions in this glass [7].

(a) Optical bandgap and Urbach energy

The optical band gap in the amorphous system is closely related to the energy gap between valence and conduction bands [6-9]. In glasses anions show much influence in the conduction band and Urbach energy gives the width of the tails of localized states within the optical band gap. The main feature of the absorption edge of an amorphous system is an exponential increase of the absorption coefficent (α) with photon energy ($h\nu$) in accordance with the empirical relation given by Hassan and Hogarth [6]

$$\alpha = \alpha_0 \exp(h\nu / \Delta E)$$

where α_0 is a constant , ΔE is the Urbach energy which indicates the width of the band tails of the localised states and ν is the frequency of the radiation. For an absorption by indirect transition, the equation takes the form

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

where B is a constant and E_{opt} is the band gap [10].Optical band gap Eo was calculated by the drawning plots between$(\alpha h\nu)^{1/2}$ versus $h\nu$(Figure2a). The optical band gap energies vary from 2.5 to 3.2 eV which is of the same order as expected for borate glasses **.**Plots were also drawn with lnα against $h\nu$(Figure2b).The value of Urbach energy E, were calculated by determining the slopes of the linear regions of these curves and taking their reciprocals. The values of optical band gaps(E_0)Urbach energy thus calculated are also presented in Table I

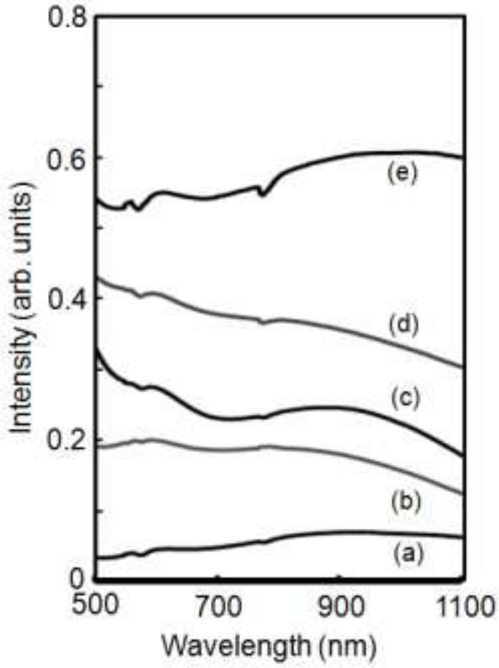


Fig1 Optical absorption spectra of Lithium Sodium borate glasses containing Vanadium

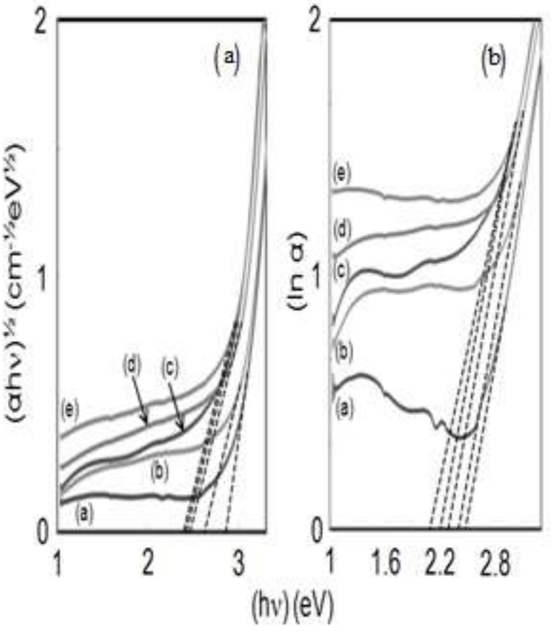
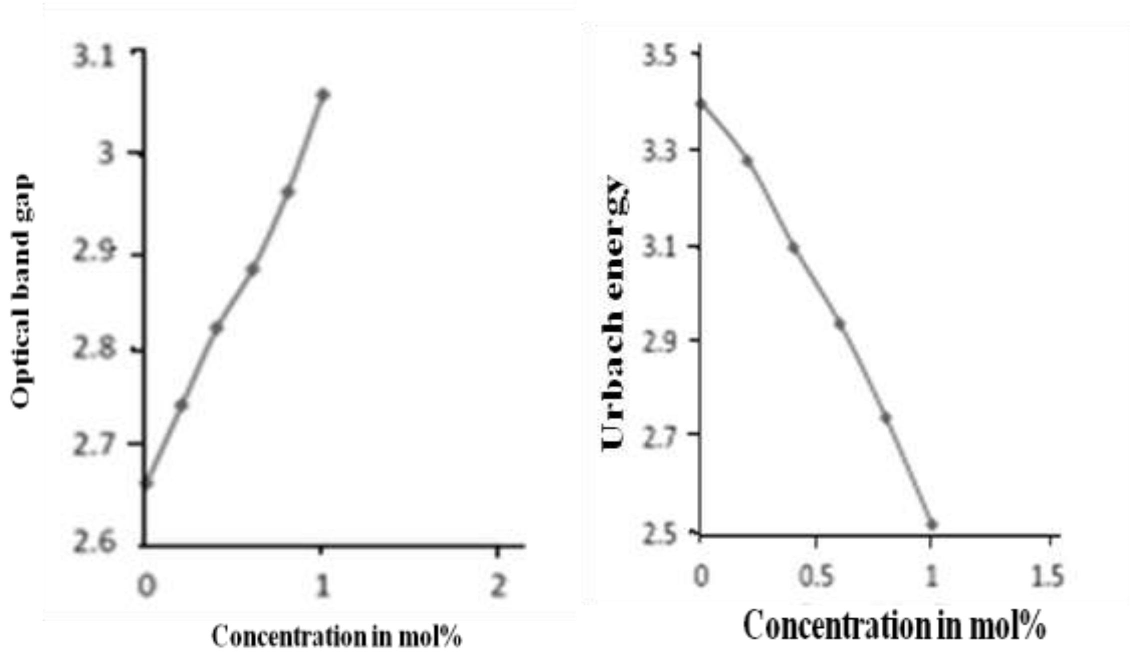


Fig2 optical band gap and Urbach energies with different concentrations

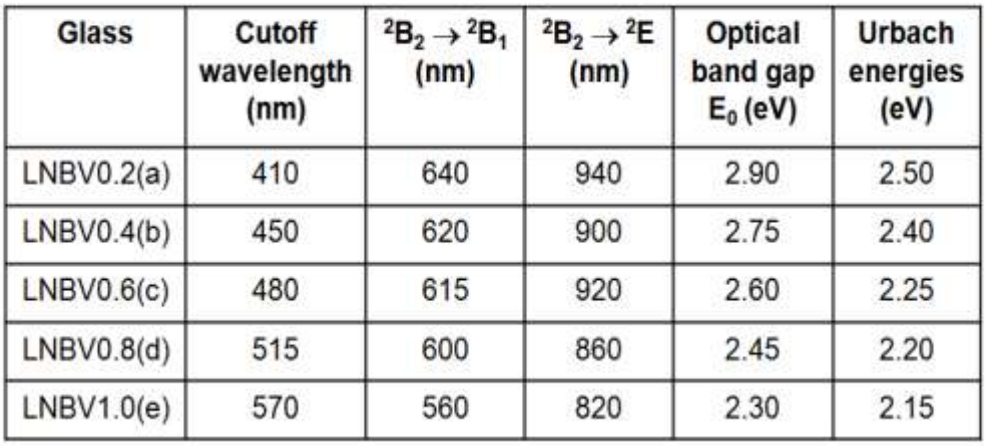
Plots of optical band gap energy and Urbach energy versus concentration are shown in figure (3a, 3b). It is observed that the band gap energy increases with increase in concentration (x) reaching maximum at x=1.0mol% and Urbach energy reaches a minimum at x=1.0 mol% concentration suggesting that the defects in this glass sample are minimum at this concentration of the dopant.



(a) **(b)**

Fig3 (a,b) Comparison of optical band energy and Urbach energy with concentration

Table I:Summary of the data on optical absorption spectra of $20Li_2O - 10\ Na_2O - (70\text{-}X)B_2O_3$: XV_2O_5



Glass	Cutoff wavelength (nm)	$^2B_2 \rightarrow {}^2B_1$ (nm)	$^2B_2 \rightarrow {}^2E$ (nm)	Optical band gap E_0 (eV)	Urbach energies (eV)
LNBV0.2(a)	410	640	940	2.90	2.50
LNBV0.4(b)	450	620	900	2.75	2.40
LNBV0.6(c)	480	615	920	2.60	2.25
LNBV0.8(d)	515	600	860	2.45	2.20
LNBV1.0(e)	570	560	820	2.30	2.15

EPR studies

The EPR spectra, recorded at room temperature for Li_2O–Na_2O_3–B_2O_3:V_2O_5 glasses under investigation are shown in Fig.4; spectra are observed to be complex made up of resolved hyperfine components arising from unpaired $3d^1$ electron whose spin is 7/2[5].

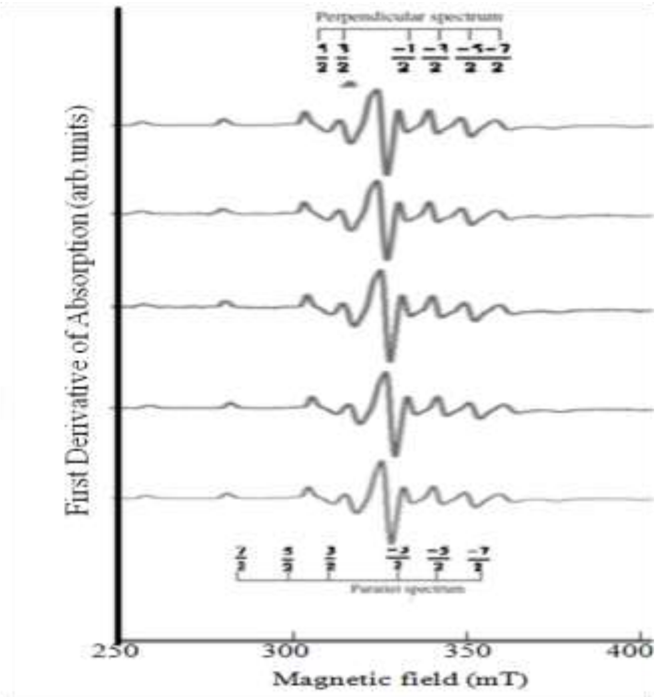


Fig 4 EPR spectra of $20Li_2O - 10\ Na_2O - (70\text{-}X)B_2O_3$ doped with XV_2O_5 glasses at room temperature

These spectra were analysed by assuming [4] that vanadium is present as a vanadyl ion in ligand field of C_4V symmetry.

The spin Hamiltonian [2] used is of the form

$$\mathbf{H(S_z I_z + A(S_x I_x + S = \beta g_{ll} B_z S_z + \beta g_{\perp}(B_x S_x + B_y S_y) + A_{lly} I_y)}$$

where the symbols have their usual meaning. The quadrupole and nuclear Zeeman interactions terms are ignored. The solutions [11] of the spin Hamiltonian are given in equations

$$B_{\parallel}(m) = B_{\parallel}(0) - mA_{\parallel} - \left\{\frac{63}{4} - m^2\right\} \frac{A_{\perp}^2}{2B_{\parallel}(0)} \qquad \text{\_\_\_\_\_\_\_\_\_\_(1)}$$

$$B_{\perp}(m) = B_{\perp}(0) - mA_{\perp} - \left\{\frac{63}{4} - m^2\right\} \frac{A_{\perp}^2 + A_{\parallel}^2}{4B_{\perp}(0)} \qquad \text{\_\_\_\_\_\_\_\_\_\_(2)}$$

where m is the magnetic quantum number of the vanadium nucleus.

$B_{\parallel}(0) = hv/g_{\parallel}\beta$ and $B_{\perp}(0) = hv/g_{\perp}\beta$.

Measurements for the $B_{\parallel}$ position were taken which correspond to a maximum in the first derivative curve of the parallel hfs component for a given m value, whereas the $B_{\perp}$ position is enclosed between the first derivative perpendicular peak and its 'zero' [12]. Spin Hamiltonian parameters of VO^{2+} ion are determined by using Eqs.(1) and (2) for each sample of different concentration and are listed in Table **II**.

Table II|: Spin Hamiltonian parameters

Glass code	**$g_{\parallel}$ ±0.001**	**$g_{\perp}$ ±0.001**	**$\lvert A_{\parallel}\rvert$ (±1.0) 10^{-4} Cm^{-1}**	**$\lvert A_{\perp}\rvert$ (±1.0) 10^{-4} Cm^{-1}**	**P**	**K (10^{-4} Cm^{-1})**
LNBV-0.2	1.9425	1.9688	18.600	6.9	13.943	0.688
LNBV-0.4	1.9470	1.9876	18.900	7.5	12.86	0.828
LNBV-0.6	1.9451	1.9610	18.400	6.8	13.378	0.729
LNBV-0.8	1.9562	1.9688	17.814	7.2	11.894	0.865
LNBV-1.0	1.9607	1.9818	17.225	6.9	11.555	0.867

The errors in g and A values are±0.001 and ± 1.0 x 10^{-4} Cm^{-1}respectively.

The values of $g_{\parallel}$ and $g_{\perp}$ along with the other data are furnished in Table II. From the values of these parameters, the dipolar hyperfine coupling parameter, $P = 2\gamma\beta\beta_N\langle r^{-3}\rangle$, and the Fermi contact interaction term K, are evaluated by using the expressions developed by Kivelson and Lee[13]:

$$A_{\parallel} = -P\left[K + \frac{4}{7} - \Delta g_{\parallel} - \frac{3}{7}\Delta g_{\perp}\right] \qquad \text{\_\_\_\_\_\_\_\_\_\_ (3)}$$

$$A_{\perp} = -P\left[K - \frac{2}{7} - \left(\frac{11}{14}\right)\Delta g_{\perp}\right] \qquad \text{\_\_\_\_\_\_\_\_\_\_ (4)}$$

Where $\Delta g_{\parallel} = g_{\parallel} - g_e$, $\Delta g_{\perp} = g_{\perp} - g_e$ and g_e (=2.0023) is the g factor of free electrons [14,15]. $A_{\parallel}$ and $A_{\perp}$ are found to be negative by the method proposed by Muncaster and Parke [16].The term- PKin Eqs. (3) and (4) is due to the s-character of the magnetic spin of the vanadium. Basically this s-character results from the partial unpairing or polarization of the inner s electrons as a result of an interaction with the unpaired d electrons [17]. The estimate of this polarization was made by Heine [17] and the contribution to the hyperfine coupling due to the term-PK is included. For transition ions, K is found to be positive [15]. From the molecular orbital theory, it can also be shown [14] that the components $A_{\parallel}$ and $A_{\perp}$ consist of the contributions $A'_{\parallel}$and $A'_{\perp}$ of the $3d_x$, 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 way:

$$A_{\parallel} = -PK - P\left(\frac{4}{7} - \Delta g_{\parallel} - \frac{3}{7}\Delta g_{\perp}\right) = -PK + A'_{\parallel} \qquad \text{\_\_\_\_\_\_\_\_\_\_}\textbf{(5)}$$

$$A_{\perp} = -PK + P\left(\frac{2}{7} + \left(\frac{11}{14}\right)\Delta g_{\perp}\right) = -PK + A'_{\perp} \qquad \text{\_\_\_\_\_\_\_\_\_\_\_}\textbf{(6)}$$

The values of $A'_{\parallel}$and$A'_{\perp}$were calculated and are given in Table III. The values of $\Delta g_{\parallel}/\Delta g_{\perp}$ which measure the tetragonality of the vanadium site [14], are also included in Table III.

Table III: The spectral parameters of vanadium ions in $20Li_2O$ – 10 Na_2O – (70-X)B_2O_3 doped with XV_2O_5 at room temperature

Glass No.	$\lvert A_{\parallel}{}' \rvert$ (10^{-4} cm^{-1})	$\lvert A_{\perp}{}' \rvert$ (10^{-4} cm^{-1})	PK (10^{-4} cm^{-1})	$\Delta g_{\parallel}$ / $\Delta g_{\perp}$
LNBV0.2	9.0009	2.6989	9.5928	1.7850
LNBV0.4	8.2439	3.1545	10.6481	1.7619
LNBV0.6	8.6461	2.9538	9.7524	1.3849
LNBV0.8	7.5152	3.0841	10.2835	1.3761
LNBV1.0	7.1847	3.1151	10.0147	2.0292

At low V_2O_5 content, the EPR spectra were observed to be asymmetrical. As the concentration of V_2O_5 is increased to 0.8 mol% an increasing degree of resolution and the intensity of signal have been observed. Further increasing the concentration beyond 0.8 mol%, suppression in the hyperfine structure has been observed i.e. hopping of a mobile electron along a V^{4+} O V^{5+} bond. Such mechanism in fact was reported in different glass systems earlier [18].As the concentration of V_2O_5 is increased up to 1.0 mol%, the degree of asymmetry in the EPR signal is decreased gradually indicating that at these concentrations of the dopant, there is a decrease in the concentration of paramagnetic borate ions in the glass network that influence the shape of the EPR signal [19].

Conclusions

- $20Li_2O$ – 10 Na_2O – (70-X)B_2O_3 mixed with different concentrations of X = V_2O_5(ranging from 0-0.1%) were synthesized by melt quenching technique.
- The color of the glasses became increasingly brown with the increase in the concentration of the dopant, indicating that the Vanadium ions exist mainly in V^{5+} state in the glass network.
- The coordination of VO^{2+} ions is nearly independent of the alkali metal ion in the glass.
- EPR and Optical absorption studies have been carried out.
- The EPR spectra was greatly influenced by the variation of concentration of V_2O_5
- The optical absorption showed a large broad band peaking at ≈800 -950nm and the intensity increases with increasing V_2O_5 concentration
- Optical band gap energies and Urbach energies are also found to be dependent on the variation of V_2O_5concentration. It is found that the defects in the glass sample with 1% concentration are minimum.
- It can be concluded that VO^{2+} ions are in an octahedral coordination with a tetragonal compression showing ligand field of fourfold symmetry.
- The analysis of EPR spectra together with optical absorption makes an impression that there is an increasing possibility of electronic conduction in the glasses containing V_2O_5 beyond 1.0 mol%.

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