

# FTIR, EPR, and Optical Absorption Spectra of Vanadium Ions Doped in ( $B_2O_3$ -ZnO-Na<sub>2</sub>O) Glasses.

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*Glasses of the composition  $xV_2O_5-(100-x)[0.5B_2O_3-0.2ZnO-0.3Na_2O]$ , where  $x = 0, 0.5, 1, 2$  and  $3$  mol% were prepared by melt quenching method. It can be seen that both density  $\rho$  and molar volume  $V_M$  were found to almost increases by doping of  $V_2O_5$ . FTIR spectra in the frequency range ( $400-2000\text{ cm}^{-1}$ ) were measured for the prepared glasses. It can be seen that studied samples contain the bands characteristic for  $B_2O_3$  [ $\delta$  (B-O-B)= $715\text{ cm}^{-1}$ ,  $\rho$  (B-O) = $1031\text{ cm}^{-1}$ ], and  $V_2O_5$  ( $\rho$  (V-O) =  $945\text{ cm}^{-1}$ ) groups. From the FTIR studies, it was observed that the glasses are made up of  $BO_3$  and  $BO_4$  groups. The Electron Paramagnetic Resonance (EPR) spectra for the glasses doped of  $V_2O_5$  ( $x \leq 3$  mol %) has been recorded on the x-band ( $\nu = 9.14\text{ GHz}$ ) at room temperature. The spin Hamiltonian parameters, dipolar hyperfine coupling parameter,  $P$  and Fermi contact interaction parameter,  $K$  have been calculated. It has been found that  $V^{4+}$  ions in these glasses exist as  $V^{2+}$  in octahedral coordination with a tetragonal distortion. Optical absorption spectra for the prepared glasses have been measured by UV-VIS spectrophotometer in the wavelength range ( $190-1200\text{ nm}$ ) at room temperature. The optical energy gap values have been calculated and show indirect transition mechanism. The optical energy gap values  $E_g$  have been calculated and were found to decreases with doping of  $V_2O_5$ . Also Urbach energy gap  $\Delta E$  values have been estimated and were found to increases with doping of  $V_2O_5$ .*

## **1. Introduction:-**

Vanadium exists in a number of oxide forms, the di-, and sesqui- and pent-oxides ( $VO_2$ ,  $V_2O_3$  and  $V_2O_5$ ). They have been processed in thin film form and applied as optical and electrical devices. Especially vanadium oxide ( $V_2O_5$ ), as a wide band gap and n-type semiconductor material, was widely investigated because of its interesting electrochemical performance [1-2], is integration in lithium secondary batteries [3], and its thermo chromic [4-6] and electro chromic properties [7-8].

Glasses containing vanadium ions have attracted much interest in solid-state chemistry and materials science in recent years, since  $V_2O_5$  is known to participate in the glass network with  $VO_5$  pyramidal structural units. Vanadium ions, when mixed in small quantities in the glass matrices, make the glasses suitable for use in memory and switching devices [8]. Several vanadate glasses show semiconducting behavior with the electrical conductivity of  $10^{-3}$  to  $10^{-5}$  ( $\Omega \text{ cm}$ )<sup>-1</sup>, which is known to be due to the electron hopping between  $V^{4+}$  and  $V^{5+}$  ions existing in the glass network, and are identified as n-type semiconductors for low values of the  $V^{4+}/V^{5+}$  ratio [9]. The vanadium ions may also exist in the glass network in  $V^{2+}$  and  $V^{3+}$  states [9]. A considerable number of spectroscopic and magnetic studies of vanadium ions in a variety of glass systems are also available in the literature. The vanadium oxide structural groups are expected to mix easily in a [ZnO- Na<sub>2</sub>O- B<sub>2</sub>O<sub>3</sub>] glass network, because some of the infrared vibration bands of the structural groups of these ions lie in the same region as those of borate structural units and are expected to occupy a variety of sites with different crystal field strengths due to site variability. EPR studies on a variety of vanadium containing glasses have been reported in the past. Paramagnetic vanadium is generally characterized by an eight the spectrum and exhibits tetragonal distorted octahedral coordination as the  $Vo^{2+}$  complex [10-11].

In the present paper we are reporting FTIR, EPR and optical absorption studies on ternary alkali borate glasses doped with  $V_2O_5$  (in mol %).

## 2. Experimental Technique:-

Glass samples of composition  $xV_2O_5-(100-x)[0.5B_2O_3- 0.2 ZnO- 0.3Na_2O]$ , where  $x = 0, 0.5, 1, 2$  and  $3$  mol% were prepared by conventional melt techniques [12]. High purity ingredients (99.99%) of chemicals are boric acid ( $H_3BO_3$ ), sodium carbonate ( $Na_2CO_3$ ), Zinc oxide (ZnO), and vanadium oxide  $V_2O_5$ . The weight quantities of these chemicals in appropriated proportions were thoroughly mixed in an agate mortar. The materials were mixed in appropriate mole percent to get the required composition. Each batch was melted in a porcelain crucible in an electrical furnace and the temperature was raised slowly to  $950^\circ\text{C}$  at which point the mixture melted. This temperature was maintained for about 1h. To obtain the homogeneity the melt was shaken frequently. The melt was then poured onto a stainless steel block and was immediately pressed by another stainless steel block at room temperature. The compositions of the glasses studied in the present investigation are given in Table (1).

Density ( $\rho$ ) of the doped glass samples with  $x = 0.5, 1, 2$  and  $3$  mol %  $V_2O_5$  were measured by Archimedes method using carbon tetrachloride  $CCl_4$  ( $\rho = 1.593 \text{ g/cm}^3$ ) as buoyant fluid. Also molar volume  $V_M$  of the prepared samples was calculated according to the relation:-  $V_M = \sum x_i * m_i / \rho$ , where  $x_i$  is the molar fraction,  $m_i$  molecular weight of  $i$ th component and  $\rho$  is the density of glasses. IR absorption spectra were recorded in the wave number range ( $400-2000 \text{ cm}^{-1}$ ) using KBr pellets with a Carl Zeiss Jena spectrometer (UR 20 model).

**Table (1):** Glasses of the compositions of  $xV_2O_5-(100-x)[0.5B_2O_3-0.2ZnO-0.3Na_2O]$ , where  $x = 0, 0.5, 1, 2$  and  $3$  mol %.

Samples	B <sub>2</sub> O <sub>3</sub>	ZnO	Na <sub>2</sub> O	V <sub>2</sub> O <sub>5</sub>
V <sub>0</sub>	50	20	30	0
V <sub>0.5</sub>	49.75	19.90	29.85	0.5
V <sub>1</sub>	49.50	19.80	29.70	1
V <sub>2</sub>	49.00	19.60	29.40	2
V <sub>3</sub>	48.50	19.40	29.10	3

EPR spectra of the doped glass samples were recorded at room temperature (300K) in the X-band ( $\gamma=9.14\text{GHz}$ ) on an EPR spectrometer (Varian E-112). Magnetic field was modulated by 100 KHz. Polycrystalline DPPH was used as a standard g marker ( $g=2.0036\pm 0.0002$ ). Time constant = 81.92 ms and sweep time = 20.97s. The optical absorption spectra of the doped glass samples were recorded at room temperature using Perkin Elmer UV- VIS spectrophotometer ( $\lambda=20$ ) over the wavelength range (190-1200 nm).

### 3. Results and Discussions:-

#### 3.1. Density and Molar Volume:-

Density  $\rho$  of composition  $xV_2O_5-(100-x)[0.5B_2O_3 - 0.2 ZnO - 0.3Na_2O]$ , where  $x = 0.5, 1, 2$  and  $3$  mol % were measured at room temperature using the Archimedes method according to the relation [12]:-

$$\rho = \rho_0 (W_{\text{air}} / W_{\text{air}} - W_{\text{Liquid}}) \quad (1)$$

where  $W_{\text{air}}$  and  $W_{\text{Liquid}}$  are the weight of the glasses in air and liquid respectively,  $\rho_0$  is the density of liquid (CCl<sub>4</sub>). The density data were used to estimate the molar volume  $V_M$  according to the relation:-

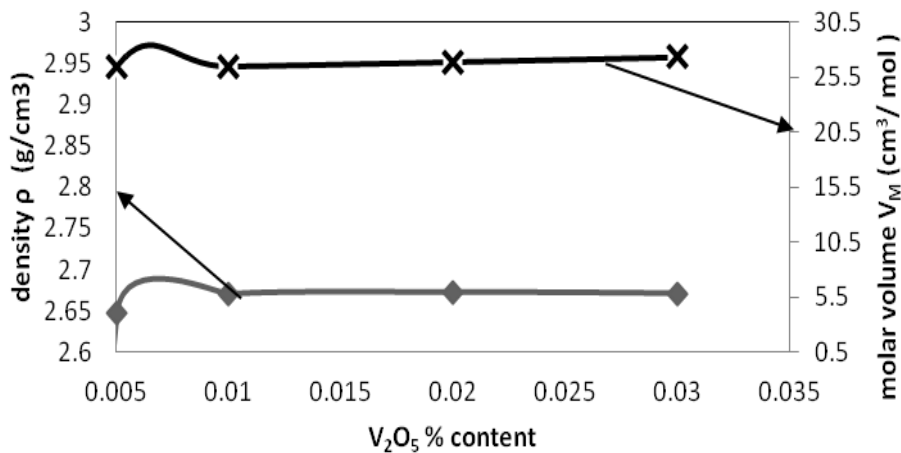
$$V_M = \sum xi * mi / \rho \quad (2)$$

Where  $xi$  is the molar fraction,  $m_i$  molecular weight of  $i$ th component and  $\rho$  is the density of the prepared glasses. The calculated values of  $\rho$  and  $V_M$  are Listed in Table (2) and are shown in Fig.(1). It can be seen that, both  $\rho$  and  $V_M$  show the same trend where  $\rho$  and  $V_M$  almost increases as  $x$  increases. In general, it is expected that the both density and the molar volume should show opposite trend to each other but in the present glasses the behavior is different. However, this anomalous behavior was reported earlier for many other glasses, for example  $LiBO_2\text{-}TeO_2$  [13],  $Li_2O\text{-}Ti_2O_3\text{-}B_2O_3$  [14] and  $TeO_2\text{-}Na_2O\text{-}B_2O_3$  [15]. The molar volume behavior reveals that an increase in the content of  $V_2O_5$  which leads to the formation of non-bridging oxygen's (NBO<sub>s</sub>) and expands (open up) the structure of the light network of  $B_2O_3\text{-}ZnO\text{-}Na_2O\text{-}V_2O_5$  glasses. The larger values of the radii and the bond length of  $V_2O_5$  compared to those of  $B_2O_3$ , ZnO and  $Na_2O$

resulted in a formation of excess free volume, which increases the overall molar volume of these glasses. This trend supports the so called open structure idea, which may be attributed to the inability of the voids of the borate network to accommodate such modifier ions without any expansion of the glass matrix.

**Table (2):** Density  $\rho$  and Molar Volume  $V_M$  of  $x V_2O_5$  (100-x)[0.5B<sub>2</sub>O<sub>3</sub>-0.2 ZnO-0.3Na<sub>2</sub>O] where  $x = 0.5, 1, 2$  and  $3$  mol %.

Samples	Density( gm /cm <sup>3</sup> )	Molar Volume (cm <sup>3</sup> /mol)
V <sub>0.5</sub>	2.647021277	26.53315
V <sub>1</sub>	2.670127986	26.51365
V <sub>2</sub>	2.672619962	26.90876
V <sub>3</sub>	2.671038603	27.34477



**Fig.(1) :** Density  $\rho$  and Molar Volume  $V_M$  as a doping of  $V_2O_5$ .

### 3.2. FTIR Absorption Spectra:

The infrared spectra of the glasses exhibited absorption peaks. The peaks are sharp, medium weak and broad. The vibration mode of the borate glasses network seems to be mainly active in three infrared regions. Fig.(2) shows the FTIR spectra in the frequency range (400-2000 cm<sup>-1</sup>) of the  $xV_2O_5$ -(100-x) [0.5B<sub>2</sub>O<sub>3</sub>- 0.2 ZnO- 0.3Na<sub>2</sub>O] where  $x = 0, 0.5, 1, 2$  and  $3$  mol % glasses. It can be seen that, the first band were centered at about 712, 713, 714, 714 and 713cm<sup>-1</sup> for samples with  $x = 0, 0.5, 1, 2$  and  $3$  mol% respectively, which corresponds to the bond-bending vibration of the B-O-B groups [16]. Second band appeared at about 1016, 1013, 1013, 1012 and 1000 cm<sup>-1</sup> for samples  $x = 0, 0.5, 1, 2,$  and  $3$  mol% respectively, which are characteristic for stretching vibrations of B-O bonds involving B<sup>4+</sup> and B<sup>3+</sup> ions respectively [17]. Another broad band centered at 1381, 1382, 1383, 1380 and 1385 cm<sup>-1</sup> which is due to the B-O stretching vibration [18]. Another peak centered at 943cm<sup>-1</sup> for sample with  $x = 0$  mol %

(free of V<sub>2</sub>O<sub>5</sub> content) and disappeared in other samples with V<sub>2</sub>O<sub>5</sub> content. This suggests that the number of V-O bonds implied in polyvanadate ions formation (network former role of V<sub>2</sub>O<sub>5</sub>) increases more rapidly than the number of BO<sub>4</sub> groups [16].

### 3.3. EPR Spectra:-

EPR spectra at room temperature for xV<sub>2</sub>O<sub>5</sub>-(100-x)[0.5B<sub>2</sub>O<sub>3</sub>- 0.2ZnO- 0.3Na<sub>2</sub>O], where x= 0.5, 1, 2 and 3 mol% glasses at dose 50 gray (GY) are shown in Fig.(3). These spectra show features very similar to those found in various alkali borate glasses doped with vanadium ion [19, 20]. The spectra show structure which is due to a hyperfine interaction of an unpaired electron with a <sup>51</sup>V nucleus whose nuclear spin is I = 7/2. These spectra were analyzed by assuming [21, 22] that vanadium is present as vandyl ion in a legend field of C<sub>4v</sub> symmetry. The axial spin Hamiltonian is of the form [19].

$$H = Bg_{\parallel} B_z S_z + Bg_{\perp} (B_x S_x + B_y S_y) + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y) \quad (3)$$

Where B is the Bohr magneton, g<sub>∥</sub> and g<sub>⊥</sub> are the parallel and perpendicular principal components of the g tensor, A<sub>∥</sub> and A<sub>⊥</sub> are the parallel and perpendicular principal components of hyperfine coupling tensor, B<sub>x</sub>, B<sub>y</sub> and B<sub>z</sub> are the components of the magnetic field and S<sub>x</sub>, S<sub>y</sub>, S<sub>z</sub>, and I<sub>x</sub>, I<sub>y</sub>, I<sub>z</sub> are the components of spin operators of the electron and nucleus respectively. The quadruple and the nuclear Zeeman interaction terms have been ignored. The solutions of the spin Hamiltonian Eq.(3) are presented in Eqs.(4) and(5) for the parallel and perpendicular orientation, respectively.

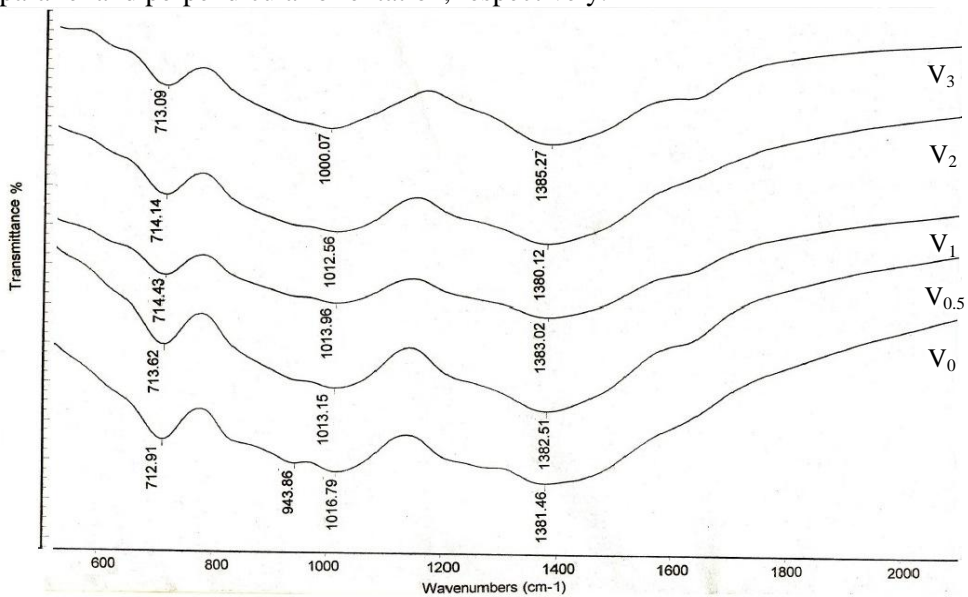


Fig. (2): FTIR spectra for xV<sub>2</sub>O<sub>5</sub>-(100-x)[0.5B<sub>2</sub>O<sub>3</sub>- 0.2ZnO- 0.3Na<sub>2</sub>O], where x= 0, 0.5, 1, 2 and 3 mol% glasses.

$$B_{\parallel}(m) = B_{\parallel}(0) - mA_{\parallel} - \{(63/4)-m^2\}A_{\perp}/2B_{\parallel}(0) \quad (4)$$

$$B_{\perp}(m) = B_{\perp}(0) - mA_{\perp} - \{(63/4)-m^2\}A_{\parallel}^2 + A_{\perp}^2/4B_{\perp}(0) \quad (5)$$

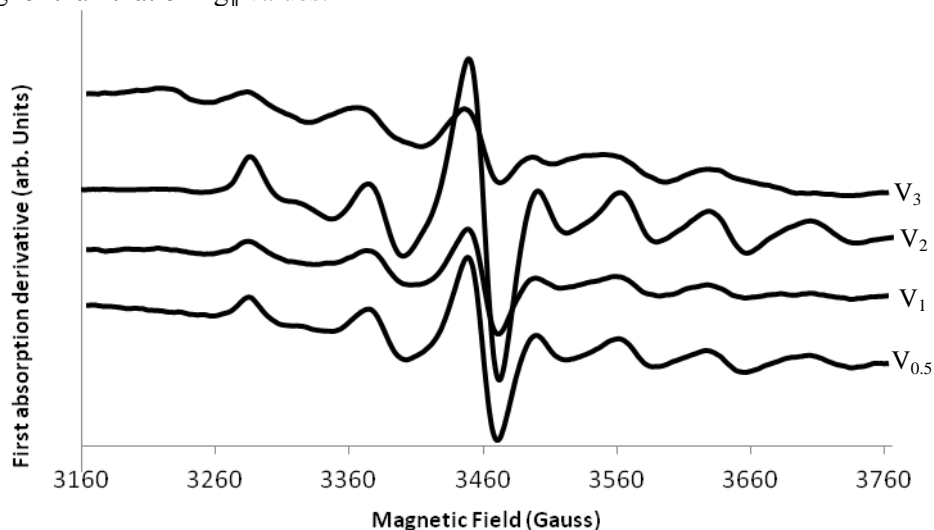
where  $m$  is the magnetic quantum number of the vanadium nucleus having values,  $\pm \frac{7}{2}$ ,  $\pm \frac{5}{2}$ ,  $\pm \frac{3}{2}$ , and  $\pm \frac{1}{2}$ ,  $B_{\parallel}(0) = h\nu/g_{\parallel}B$  and  $B_{\perp}(0) = h\nu/g_{\perp}B$ .

Where  $h$  Planck's constant,  $\nu$  is the frequency of the spectrometer and  $B$  is the Bohr magneton. Measurements for the  $B_{\parallel}$  position were taken which correspond to a maximum in the first derivative curve of the parallel hyperfine structure (HFS) component for a given  $m$  value, where as the  $B_{\perp}$  position is enclosed between the first derivative perpendicular peak and its zero [19]. Spin Hamiltonian Parameter of the  $V_2O_5$  ion determined by using Eqs. (4) and (5) for samples with  $x = 0.5, 1, 2$  and  $3$  mol % are given in Table (3). From the values of these parameters, the dipolar hyperfine coupling parameter,  $P = 2\nu\Delta B_e B_N < r^{-3} >$  and the Fermi contact interaction term,  $K$  are evaluated using the expressions developed by Kivelson and Lee [23]

$$A_{\parallel} = -P[K+4/7-\Delta g_{\parallel}-3/7\Delta g_{\perp}] \quad (6)$$

$$A_{\perp} = -P[K-2/7-11/4\Delta g_{\perp}] \quad (7)$$

where  $\Delta g_{\parallel} = g_{\parallel} - g_e$ ,  $\Delta g_{\perp} = g_{\perp} - g_e$  ( $g_e = 2.0036$ ) is the factor of free electron,  $A_{\parallel}$ ,  $A_{\perp}$  are found to be negative by the method proposed by Muncaster and Parke[24]. Fig.(4) show the relation between  $\Delta g_{\parallel}$  and  $\Delta g_{\perp}$  where  $\Delta g_{\perp}$  values are always higher than that of  $\Delta g_{\parallel}$  values.



**Fig.(3):** EPR spectra of  $xV_2O_5 - (100-x)[0.5 B_2O_3 - 0.2 ZnO - 0.3 Na_2O]$  where  $x = 0.5, 1, 2,$  and  $3$  mol % at room temperature.

Some physical parameters were estimated and listed in Table(4) such as magnetic field in Gauss  $H_0$ , peak width  $\Delta H$ , factor depending on experimental condition  $K$ , intensity per weight  $A$ , modulation amplitude value  $H_m$  and receiver gain  $G_e$ .

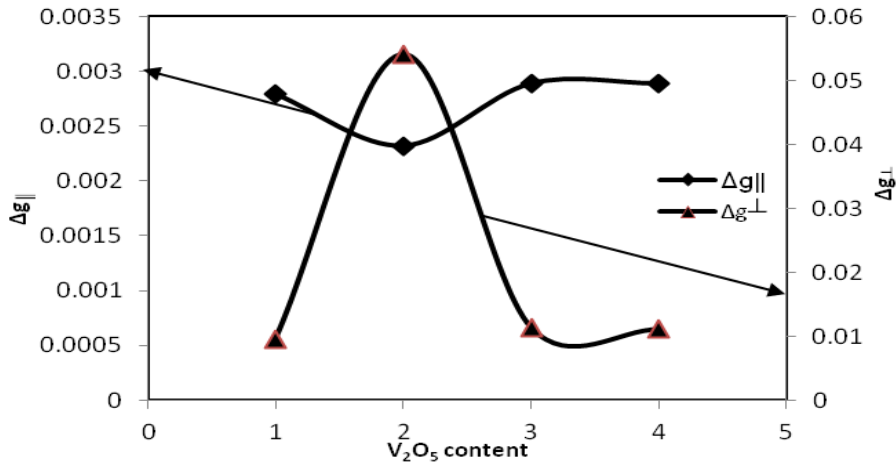


Fig.(4): Relation between  $\Delta g_{||}$  and  $\Delta g_{\perp}$  as a function of  $V_2O_5$  content.

Table (3): Spin Hamiltonian parameters of  $xV_2O_5 - (100-x)[0.5 B_2O_3 - 0.2 ZnO - 0.3 Na_2O]$   $x = 0.5, 1,$  and  $3$  mol % glasses at room temperature.

Sample	Peak Height(H)	Weight, gm (W)	H/W	$g_{  }$	$g_{\perp}$	A//	$\Delta g_{  }$	$\Delta g_{\perp}$	$\Delta g_{  } / \Delta g_{\perp}$
$V_{0.5}$	2772	0.2746	10094.6832	2.00639	2.01322	0.042	0.00279	0.00962	0.29002079
$V_1$	1587	0.2253	7043.94141	2.00592	2.05768	0.0416	0.00232	0.05408	0.04289941
$V_2$	1117	0.2526	4422.0111	2.00649	2.01503	0.0429	0.00289	0.01143	0.25284339
$V_3$	1121	0.2889	3880.23538	2.00649	2.01469	0.0416	0.00289	0.01109	0.26059513

Table (4):  $H_0$ , is magnetic field in Gauss,  $\Delta H$  is peak width, K is factor depending on experimental condition =1013, A is intensity per weight,  $H_m$  is modulation amplitude value and Ge is receiver gain.

Sample	$H_0$	$\Delta H$	A	K	$H_1 = H_0 * \Delta H * A * k$	$H_m$	Ge	root PH	$H_2 = H_m * Ge * \text{root PH}$	$H_3 = H_1 / H_2$
$V_{0.5}$	3460	21.9	10094.683	1.00E+13	8.37581E+22	8	17800	2.522	359132.8	2.33223E+17
$V_1$	3460	23.02	7043.9414	1.00E+13	6.45762E+22	8	17800	2.525	359560	1.79598E+17
$V_2$	3460	27.1	4422.0111	1.00E+13	5.61829E+22	8	17800	2.522	359132.8	1.56441E+17
$V_3$	3460	26.73	3880.2354	1.00E+13	4.70654E+22	8	17800	2.522	359132.8	1.31053E+17

### 3.4. Optical absorption Spectra:-

Optical absorption spectra, A, were recorded on a UV-VIS double beam spectrophotometer at room temperature in the wavelength range (200-1100 nm). The optical absorption coefficient  $\alpha(\omega)$  was calculated using the absorbance A, according to the equation:-

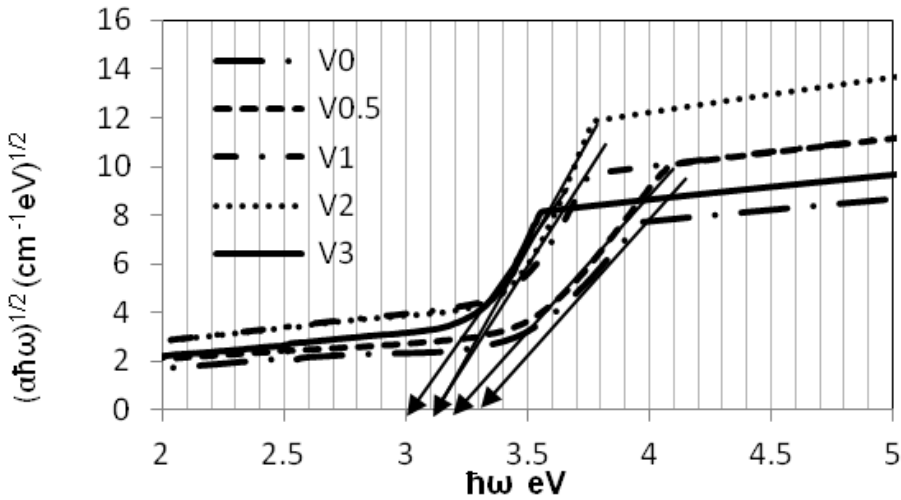
$$\alpha(\omega) = 2.303A/d \tag{8}$$

where d is the thickness of the sample.

The relation between the optical absorption coefficient  $\alpha(\omega)$  and optical band gap energy  $E_g$  in many amorphous materials are related as [25].

$$\alpha h\omega = B (h\omega - E_g)^r \tag{9}$$

where B is an energy independent constant and r is a constant determines type of the optical transition and can have different values; 1/3, 1/2, 2, and 3 corresponding to direct forbidden, direct allowed, indirect allowed and indirect forbidden transitions respectively. Change in  $(\alpha\hbar\omega)^{1/r}$  on photon energy  $\hbar\omega$  called Tauc's plot [26] has been plotted for  $r = 1/3, 1/2, 2,$  and  $3,$  but  $r= 2$  is found to be most suitable. Thus, the present glass system shows indirect allowed transitions. This is expected behavior. Since in amorphous system; indirect transition is the possible one due to lack of translation symmetry [27]. The optical band gap energies of different glass samples are estimated by extrapolation of linear region to meet  $\hbar\omega$  axis i.e.  $(\alpha\hbar\omega)^{1/2} = 0$ . The values of  $E_{g.}$  are listed in Table(5) and shown in Fig.(5). It can be seen that, the values of optical band gap were found to decrease gradually with increase of the concentration of  $V_2O_5$ .



**Fig.(5):** Relation between  $(\alpha\hbar\omega)^{1/2}$  and photon energy  $\hbar\omega$  for  $xV_2O_5 - (100-x)[0.5B_2O_3-0.2ZnO-0.3Na_2O]$  where  $x = 0, 0.5, 1, 2$  and  $3$  mol % glasses.

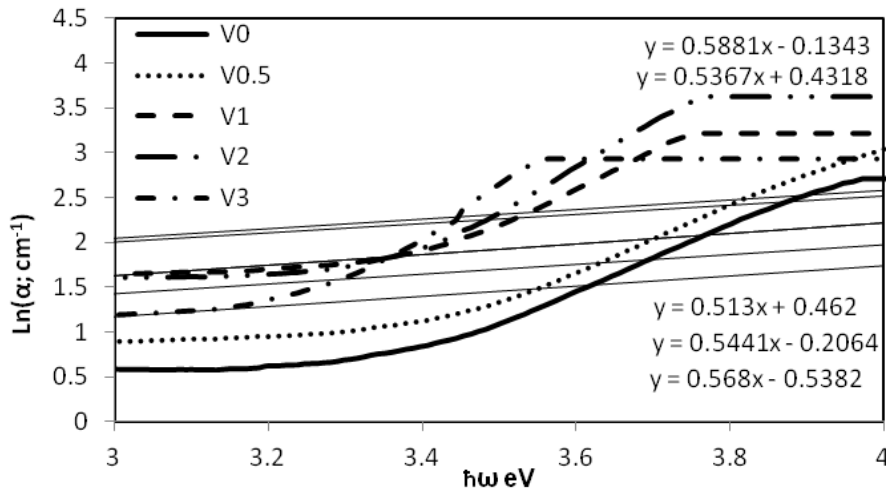
The absorption coefficient  $\ln(\alpha)$  of the optical absorption near the band edge shows an exponential dependence on the photon energy  $\hbar\omega$  and obeys the empirical relation (Urbach) relation [28]:

$$\ln\alpha = C + \hbar\omega/\Delta E \tag{10}$$

where C is a constant and  $\Delta E$  is the Urbach energy. Urbach energy is calculated from the inverse slope of the  $\ln\alpha$  and photon energy  $\hbar\omega$  as shown in Fig.(6). The calculated values of  $\Delta E$  are listed in Table (5). Urbach energy which corresponds to the width of localized state, is used to characterize the degree of disorder in amorphous and crystalline systems. Materials with large  $\Delta E$  would have greater tendency to convert weak bonds into defect. It can be seen that, the doping of  $V_2O_5$  leads to increase of  $\Delta E$  up to 1 mol % then it starts to decrease again with doping of  $V_2O_5$  up to 3 mol %.



The increase in electronic polarizability with doping of  $V_2O_5$  (in the mol %) indicates that the electron cloud is more easily deforming with concentration of  $V_2O_5$ . The  $B_2O_3$  is a strong acidic oxide with low optical basicity whereas  $V_2O_5$  is an oxide with significant optical basicity. The increase in the optical basicity of the glasses with increase in  $V_2O_5$  concentration indicates the acid- base properties of  $V_2O_5$  have significant effect. Low optical basicity means a reduced ability of oxide ions to transfer electrons to the surrounding cautions. On the other hand Zinc Sodium Borate glasses doped with  $V_2O_5$  possess high optical basicity which means high donor ability of oxide ions [29]. The optical band gap energy of the glasses is decreasing with the doping of vanadium ions whereas the Urbach energy values are increasing.



**Fig.(6):** Relation between  $\ln(\alpha)$  and photon energy ( $\hbar\omega$ ) for  $xV_2O_5$  (100-x)[ $B_2O_5$ -ZnO- $Na_2O$ ],  $x = 0, 0.5, 1, 2$  and  $3$  mol %

**Table (5):** Optical energy gap  $E_{g.}$  and Urbach energy  $\Delta E$  as a doping of  $V_2O_5$  content

Sample name	$E_{g.}$ eV	$\Delta E$ eV
$V_0$	3.32	1.76
$V_{0.5}$	3.22	1.84
$V_1$	3.18	1.94
$V_2$	3.12	1.86
$V_3$	3.05	1.7

**Conclusion:**

Glassy system of composition  $xV_2O_5$ -(100-x)[0.5 $B_2O_3$ -0.2ZnO- 0.3 $Na_2O$ ], where  $x = 0, 0.5, 1, 2$  and  $3$  mol% were prepared by melt quenching method. . No well defined trend was observed for both density and molar volume  $V_M$ , however  $\rho$  and  $V_M$  show the same trend. The obtained spectra were analyzed and assigned. E.P.R. spectra were obtained and analyzed. The dependence of  $g_{||}$  and  $g_{\perp}$  were discussed. The optical energy gap values  $E_{g.}$  have been calculated and were found to decreases with doping of  $V_2O_5$ . Also Urbach energy gap  $\Delta E$  values have been estimated and were found to increases with doping of  $V_2O_5$ .

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