Physical and Spectral Properties of VO^{2+} ions doped K_2O-Na_2O- ZnO-B_2O_3 Potassium Zinc Borate Glasses

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Abstract : K_2O-Na_2O- ZnO-B_2O_3 (KNZB) glasses of VO^{2+} ions are prepared by conventional melt quenching technique and investigated by X-ray diffraction and Optical absorption spectroscopic techniques. The XRD spectra of the glass samples reveal an amorphous nature with different compositions within the glass matrix. The Optical absorption spectra of these glasses are recorded at room temperature. Physical parameters, Urbach energies, direct and indirect band gaps are calculated. Various significant physical properties (Density, Ion concentration, Inter-ionic separation and Polaron radius) of these glass samples have been evaluated.

***IndexTerms* - Borate glasses; XRD; Optical absorption; Urbach energy.**

I. INTRODUCTION

Borate glasses with alkali ions are considered as important class of materials in microelectronics, optics and optical fibers due to its scientific and technological applications [1-3]. Borate glasses are very important optical materials because of their low melting point, high transparency, and high thermal stability [4]. It is generally used to make insulating and dielectric materials.

Na_2O and K_2O are most the common fluxes, reduces the processing temperatures and change the properties of glasses also. Viscosities of melts containing a mixture of alkali oxides are lower than those of corresponding melts containing the same total molar concentration of single alkali oxide [5]. Modifier ions are not simply filler for predetermined interstices, but modify the interstices actually that are formed. They change the free volume of the network [5]. In mixed alkali compounds if concentration of an alkali is more, its diffusivity is also more.

ZnO in glass structures is expected to act as an intermediate oxide either as network former or as network modifier. As former, ZnO enters the network with ZnO_4 structural units and as network modifier, zinc ions are octahedrally coordinated and behaves like any other conventional alkali oxides. [6 - 8]. Dual role of ZnO in zinc borate glasses was reported by Cetinka Ya Colak et al. [9]. Yao et al. [10] have prepared copper- lead and copper zinc borate glasses and discussed that the addition of ZnO that enhances the network structure. The elastic properties and spectroscopic studies on Na_2O-ZnO- B_2O_3 glasses have indicated that the Zn^{2+} ions incorporated into the network act as a former [11].

Now a days transition metal ions are being greatly used to probe the glass structure since their outer d-electron orbital function have a broad radial distribution due to their high sensitive response to the changes in the surrounding actions. Borate glasses are generally insulating in nature and the addition of transition metal such as V_2O_5, Fe_2O_3, and WO_3 etc. makes these glasses semiconducting in nature. Semi-conducting transition metal oxide such as (V_2O_5) based glasses have gained much interest in solid state chemistry and material science because of their applications as memory and switching devices. Among transition metals, V_2O_5 is an important semiconductor whose electrical conductivity is due to the electron hopping between V^{5+} and V^{4+} ions [12]. The semiconducting nature of V_2O_5 is due to two valence states V^{5+} and V^{4+} of vanadium [13]. This oxide is classified as a conditional glass-former and can enter the same network either as a network former or as a network-modifier, depending on its concentration. Vanadium oxide in oxide glasses play an important role in changing the structure, electrical, magnetic and optical properties which depends on the situation and quantity of that oxide. Vanadium oxide in oxide glasses play an important role in changing the structure, electrical, magnetic and optical properties which depends on the situation and quantity of that oxide. Vanadium belongs to the unfilled '3d' elements and possesses many valency states. The V^{2+}, V^{3+}, V^{4+} and V^{5+} states are the frequent valency states of vanadium in oxide glass [14]. The interactions between them can be described in terms of reactions [15].

$$2\,O^{2-} + 4\,V^{5+} \text{ ------->} \quad 4V^{4+} + O_2$$
$$2\,O^{2-} + 4\,V^{4+} \text{ ------->} \quad 4V^{3+} + O_2$$
$$2\,O^{2-} + 4\,V^{3+} \text{ ------->} \quad 4V^{2+} + O_2$$

In the present investigation, X-ray Diffraction (XRD), UV-visible absorption, Fourier transform infrared (FT-IR) absorption techniques are used for the characterization of V_2O_5 doped KNZB glasses.

II. EXPERIMENTAL

2.1. Glass Preparation

Series of V_2O_5 doped K_2O-Na_2O-ZnO-B_2O_3 (KNZB) glasses are prepared by melt-quenching method using analar grade chemicals of K_2CO_3, Na_2CO_3, ZnO, B_2O_3 and V_2O_5 as starting materials with 99.9 % purity. The compositions of all the glass samples are given in Table 3.1. Appropriate amounts in mol % of chemicals in powder form are weighed using a digital balance having sensitivity of ±0.0001g, ground to fine powder and mixed thoroughly. The batches are melted in silica crucibles in an electrical furnace at a temperature of 900 ^{0}C for 10 minutes. The melts are then poured on a polished brass plate and pressed quickly with another brass plate and annealed at 350 ^{0}C temperature. The glasses are then ground and optically polished. As a result transparent glasses are obtained.

Table 3.1 Composition of glasses (mol %) studied in the present work

Glass code	**K_2O (mol%)**	**Na_2O (mol%)**	**ZnO (mol%)**	**B_2O_3 (mol%)**	**V_2O_5 (mol%)**
V_0	20	15.0	5	60	0
V_1	20	14.8	5	60	0.2
V_2	20	14.6	5	60	0.4
V_3	20	14.4	5	60	0.6
V_4	20	14.2	5	60	0.8
V_5	20	14.0	5	60	1.0

2.2. Characterization techniques

The amorphous nature of the glasses was confirmed by X- ray diffraction studies carried out by XRD-6100 SHIMADZU X-Ray diffractometer in the scanning range of 10-70^0 (2θ) using CuKα radiation having a wavelength of 1.5406 Å at room temperature. The density (ρ) of the glass samples was determined to an accuracy of ±0.0001, by standard principle of Archimedes using o-Xylene (99.9% pure) as the buoyant liquid. Average molecular weight (M), various physical parameters such as manganese ion concentration (N_i), mean manganese ion separation (r_i), the polaron radius (r_p) and optical basicity (Λ th) are evaluated. The optical UV-Visible absorption spectra of prepared glass samples are recorded using JASCO V-670 UV-Vis-NIR Spectrophotometer in the wavelength region of 200-2000 nm.

III. RESULTS AND DISCUSSION

3.3.1 Physical Parameters

Depending on the glass density 'd' and calculated average molecular weight ($\overline{M}$), various physical parameters such as dopant ion concentration (N_i), mean dopant ion separation (r_i) , polaron radius (r_p) and molar volume (V_m) are evaluated using conventional formulae.

The values are furnished in Table 3.2. The density (d) of the glasses is determined by standard principle of Archimedes using o-Xylene (99.99% pure) as the buoyant liquid. A direct reading balance (capacity 100 gm, readability 0.1mg) is used for weighing. The average errors in these physical parameters are calculated and given below

Density (g/cm^3)	± 0.001
Molar volume (V_m), cm^3/mol	± 0.001
Dopant ion Concentration, N_i (10^{21}/cm^3)	± 0.001
Inter-ionic distance of Dopant ions, r_i (Å)	± 0.001
Polaron radius, r_p(Å)	± 0.001

The density values of KNZB glasses are observed that the density decreases by varying concentration of V_2O_5 and B_2O_3 in KNZB glasses from V_0 - V_5. The molar volume, Inter ionic and Polaron radius distances decreases from V_0 - V_5.

Table 3.2. Physical parameters of V_2O_5 doped KNZB glasses.

Glass Code	**Density (g/cm^3)**	**Avg. Mol. Wt. (M) (g/mol)**	**Molar Volume (V_m) (cm^3/mol)**	**Transition metal ion conc. N_i (10^{21} ions/cm^3)**	**Inter ionic distance r_i (Å)**	**Polaron radius r_p(Å)**
V_0	2.9386	73.9788	25.1748	-	-	-
V_1	2.6611	74.2186	27.8902	4.3184	6.1408	2.4743
V_2	2.4358	74.4584	30.5684	7.8800	5.0253	2.0248
V_3	2.4343	74.6982	30.6857	11.7749	4.3956	1.7711
V_4	2.4234	74.9380	30.9227	15.5795	4.0039	1.6133
V_5	2.4145	75.1778	31.1360	19.3410	3.7254	1.5011

3.3.2 X-Ray Diffraction (XRD) Studies

The amorphous nature of these glasses is confirmed by the X-ray diffraction technique. Figure 3.1 shows the X-ray diffraction spectra of KNZB glasses. X-ray diffraction is a useful method to detect readily the presence of crystals in a glassy matrix if their dimensions are greater than typically 100nm. The XRD pattern of the present glass system does not reveal any discrete or sharp peaks, give characteristic humps of the amorphous materials.

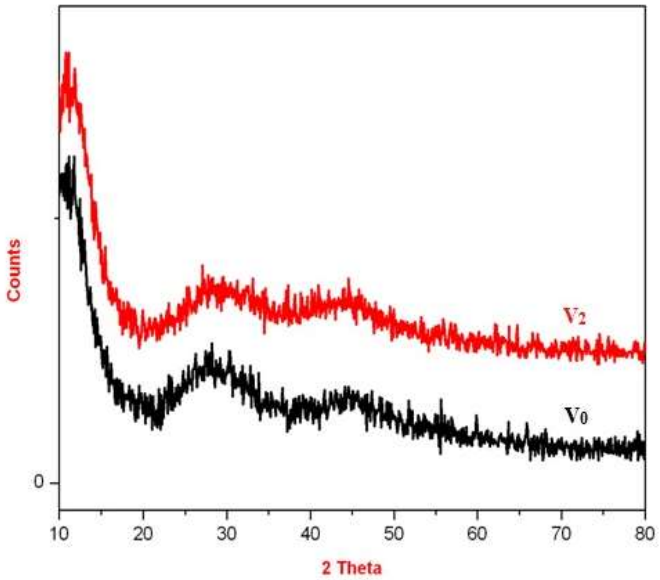

Figure 3.1. XRD pattern for undoped and V_2O_5 doped KNZB glasses

3.3.3 Fourier Transform Infrared (FT-IR) Spectroscopy

An infrared transform spectrum of glasses is very useful for qualitative identification of glass forming structural units. IR spectral investigations were important for the structural elucidation and identification of ligands field. Figure 3.2 shows the FT-IR spectra of the V_2O_5 doped K_2O-Na_2O-ZnO-B_2O_3 glass samples.

According to the IR studies conducted on borate glasses in the past, the infrared spectra of borate glasses are classified in the spectral regions as follows [16-18]:

(a) The region 600-800 cm^{-1} is assigned to bending vibrations of various borate segments.
(b) The infrared bands from 800-1200 cm^{-1} are assigned to B-O stretching of tetrahedral BO_4 units.
(c) The IR bands from 1200-1600 cm^{-1} are due to B-O stretching vibrations of BO_3 units.
(d) The near infrared bands in region 3000-4000 cm^{-1} are due to O-H vibrations of the water groups.

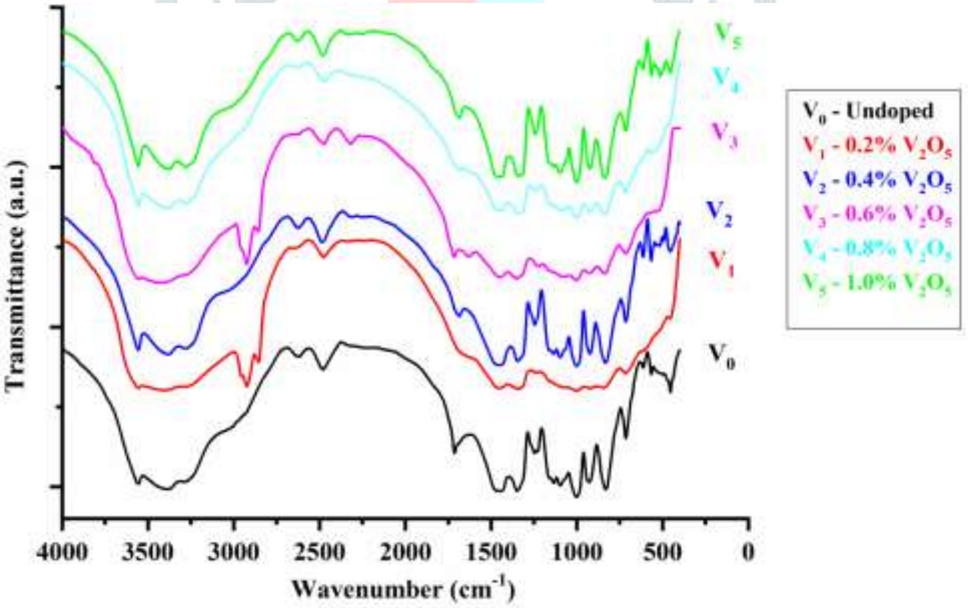

Figure 3.2. FT-IR spectra of undoped and V_2O_5 doped KNZB glasses

All samples in present system (KNZB glass system) show bands in the region 3200 - 3600 cm^{-1} which are attributed to O–H vibrations of water group [19]. Absorption band around 2480 cm^{-1} indicates the presence of B-H units [20]. The bands located at 2855 and 2924 cm^{-1} substantiate the presence of hydrogen bonding and IR absorption band at 3426 cm^{-1} point to the O-H stretching vibrations and confirm the presence of OH^- groups in the glass composition [21-23].

Absorption band around at 565 cm^{-1} is due to ZnO tetrahedron and V_2O_5 in glass matrix, absorption band around at 714 cm^{-1} is assigned to B-O-B bending vibrations [23-29], band around 838 cm^{-1} suggests the formation of tetrahedral coordination of Zn [24].

The absence of the band at 806 cm^{-1} signifies that no boroxol ring is present in the glasses under study. This corresponds to the progressive substitution of boroxol ring by BO_3 and BO_4 groups and band near 1000 - 1200 cm^{-1} interpreted as stretching vibrations of B-O bonds in BO_4 units from pentaborate groups and V = O symmetric groups [27,29]. Band around 1240-1350 cm^{-1} B-O stretching vibrations of $(BO_3)^{3-}$ units in metaborate chains and orthoborates [26]. Bands around 1448-1466 cm^{-1} shows B-O vibration of borate group [21, 22]. Band around 1632 cm^{-1} is attributed to the bending vibration of H-OH groups [28]. Various peak positions and their corresponding frequencies in FT-IR spectra of undoped and V_2O_5-doped KNZB glasses are given in the Table 3.3.

Table 3.3 Assignment of various peak positions of FT-IR spectra of undoped and V_2O_5-doped KNZB glasses.

Vibrational Frequency (cm^{-1})						Assignment of bands
V_0	**V_1**	**V_2**	**V_3**	**V_4**	**V_5**	
3556	3555	3557	3554	3556	3556	O-H stretching
3376	-	3378	-	3381	3373	O-H stretching
3283	3280	3282	-	3282	3278	O-H stretching
2478	2476	2485	2472	2480	2479	B-H unit presence
-	-	1685	1632	1683	1686	Bending vibration of H-OH groups
1448	1456	1451	1451	1444	1466	B-O vibration of borate group
1348	1349	1346	1353	1347	1343	B-O stretching vibrations of $(BO_3)^{3-}$ units in metaborate chains and orthoborates
1246	1244	1245	-	1243	1242	B-O stretching vibrations of $(BO_3)^{3-}$ units in metaborate chains and orthoborates
1133	-	1134	-	1133	1135	vibrations of B-O bonds in BO_4 units from pentaborate groups
1096	-	1095	-	1096	1100	vibrations of B-O bonds in BO_4 units from pentaborate groups
1002	996	999	1003	1003	1000	BO_4 Stretching of B-O bonds and V=O symmetric groups
927	919	922	925	924	924	B-O stretch in BO_4 units from diborate groups
830	849	833	838	836	837	Tetrahedral coordination of Zn.
714	716	714	716	716	714	B-O-B bending vibrations
612	-	613	-	-	615	Bending O-B-O linkage
565	-	566	-	566	565	ZnO tetrahedron and V_2O_5
454	455	454	-	-	455	Vibrations due to Zn

3.3.4 Optical Absorption Studies

The study of the Optical absorption spectra and in particular 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 photon energy greater than the band gap energy will be absorbed. The optical absorption spectra of V_2O_5 doped KNZB glasses are shown in Figure 3.3.

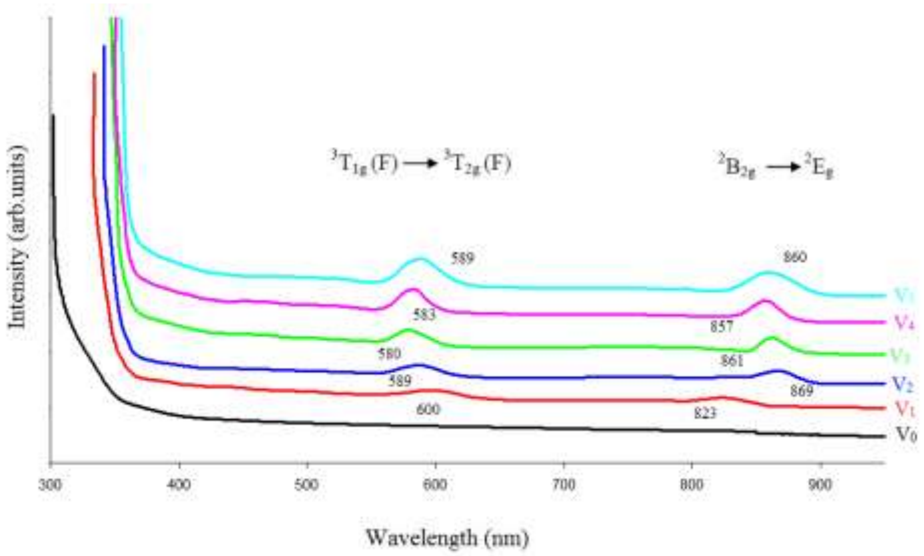

Figure 3.3. Optical absorption spectra of V_2O_5 doped KNZB glasses.

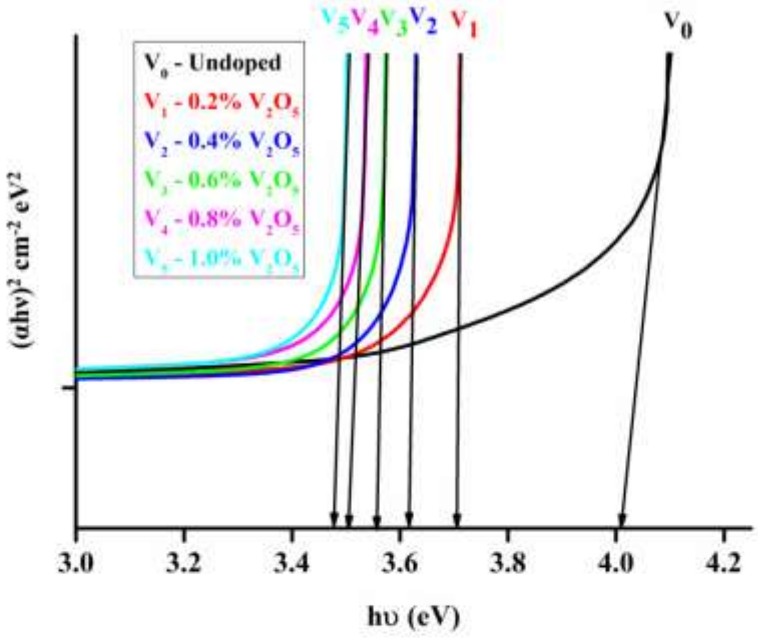

Figure 3.4. A plot between $(\alpha h\nu)^2$ and hν for V_2O_5 doped KNZB glasses

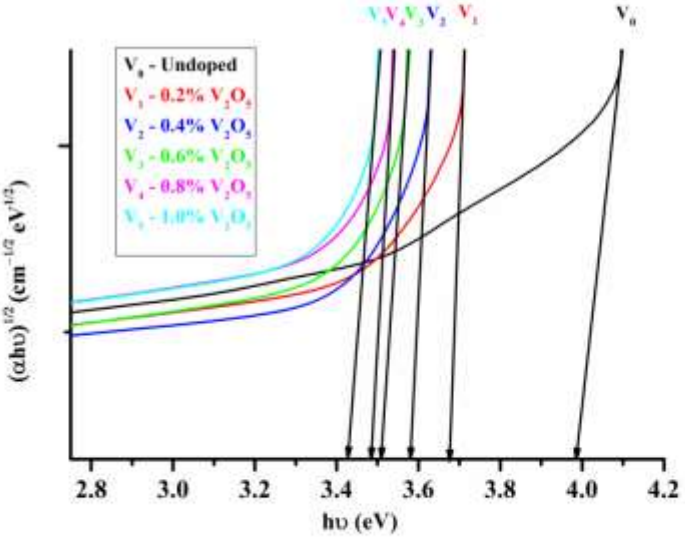

Figure 3.5. A plot between $(\alpha h\nu)^{1/2}$ and hν for V_2O_5 doped KNZB glasses

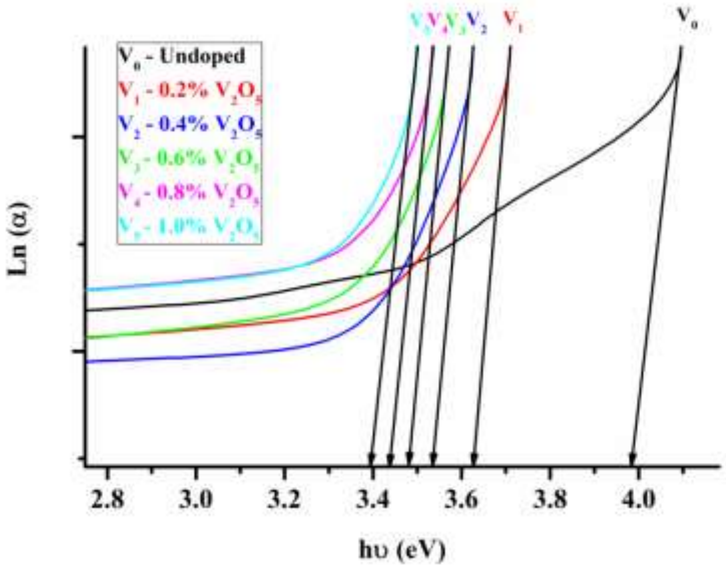

Figure 3.6. A plot between Ln (α) and hν for V_2O_5 doped KNZB glasses

The absorption coefficient, below and near the edge of each curve is determined at different wavelengths using the formula.

$$\alpha(\nu) = (1/d)\ \ln(I_0/I_t) \qquad (3.1)$$

where I_0 and I_t are intensities of the incident and transmitted beams, respectively and ‘d’ corresponds to the thickness of sample. The factor $\ln(I_0/I_t)$ is absorbance [30]. Optical band gaps are calculated using absorption spectra for direct and indirect transitions for V_1, V_2, V_3, V_4, V_5 glass samples from the following equation.

For direct transitions

$$\alpha(\nu) = B(h\nu - E_{opt})^n / h\nu \qquad (3.2)$$

where n = ½ for allowed transition, B is a constant and E_{opt} is direct optical band gap. Relation (3.2) is also used for indirect transitions. In this equation, where n = 2 for allowed transition, B is a constant and E_{opt} is indirect optical band gap. Ln(α) are plotted as a function of photon energy. Urbach energy value (ΔE) are calculated by taking the reciprocal of the slopes of linear portion in the lower photon energy region of the curve as stated with following relation [30].

$$\alpha(\nu) = \alpha_0 \exp(h\nu/\Delta E) \qquad (3.3)$$

using equation (3.2) and (3.3) and by plotting $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ as a function of energy hν, optical band gaps for indirect and direct transitions are obtained. The respective values of E_{opt} are obtained by extrapolating between $(\alpha h\nu)^{1/2}$ and hν for indirect transitions between $(\alpha h\nu)^2$ and hν for direct transitions [31]. Direct, indirect optical band gap values and Urbach energies of V_0, V_1, V_2, V_3, V_4, V_5 glass samples from Figure 3.4-3.6 are given in Table 3.4.

The Optical absorption spectra of the V_2O_5 doped KNZB glasses recorded at room temperature in the wavelength range from 200 nm to 1200 nm. In the KNZB glass matrix, V_0 has no absorption band because there is no presence of transition metal ion.

Table 3.4. Summary of the numerical on optical absorption spectra of V_2O_5 doped KNZB glasses

Glass code	**Cut-off wavelength (nm)**	**$^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ Band positions of V^{3+} ions (nm)**	**$^2B_{2g} \rightarrow {}^2E_g$ Band positions of V^{4+} ions (nm)**	**Direct band gap (eV)**	**Indirect band gap (eV)**	**Urbach Energy (eV)**
V_0	302	-	-	4.007	3.986	0.2509
V_1	334	600	823	3.707	3.677	0.2757
V_2	341	589	869	3.619	3.581	0.2828
V_3	347	580	861	3.557	3.509	0.2874
V_4	350	583	857	3.505	3.484	0.2909
V_5	354	589	860	3.477	3.428	0.2946

In general, V^{4+} ion belongs to d^1 configuration with ^2D as the ground state. In the presence of pure octahedral crystal field, the ^2D state splits into $^2T_2$ and ^2E, while an octahedral field with tetragonal distortion further splits the $^2T_2$ level into ^2E and $^2B_2$; among these, the $^2B_2$ will be the ground state. Hence, for the vanadyl ions 3 bands are expected, on the basis of energy level scheme for molecular orbitals of VO^{2+} ion in a ligand field of C_{4v} symmetry provided by Ballhausen and Gray [32] corresponding to the transitions $^2B_{2g} \rightarrow {}^2E_g$ ($d_{xy} \rightarrow d_{yz-zx}$), $^2B_{2g} \rightarrow {}^2B_{1g}$ ($d_{xy} \rightarrow d_{x^2-y^2}$) and $^2B_{2g} \rightarrow {}^2A_{1g}$ ($d_{xy} \rightarrow d_{z^2}$). These bands were observed in the region 1000-877, 714-588 and 434-374 nm respectively [33, 34]. However, the recent spectroscopic studies on gamma irradiated V_2O_5 doped sodium phosphate, lead phosphate, zinc phosphate and bismuth borate glasses [35 - 38] have concluded that the band at ~ 580-680 nm resulted to V^{3+} ions, with d^2 configuration, assigned to $^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ transition. Generally, Vanadium is believed to exists in three possible oxidation states (V^{3+}, V^{4+} and V^{5+}) depending upon the composition and glass melting atmospheric conditions [36]. In the present investigation the absorption band observed at ~ 600 nm is ascribed to trivalent vanadium (V^{3+}) ions and the another absorption band at ~ 823 nm is due to the characteristic $^2B_{2g} \rightarrow {}^2E_g$ transitions of tetravalent vanadium VO^{2+} ions in tetragonally distorted octahedral sites. Hence, The hike in the intensity of these two bands with increase in the concentration of

V_2O_5 up to 1.0 mol% suggest increasing presence of vanadyl (V^{4+}) and V^{3+} ions up to V_5. The observed blue shift in $^3T_{1g}(F)\rightarrow{}^3T_{2g}(F)$ and red shift in $^2B_{2g}\rightarrow{}^2E_g$ transitions is explained as follows: whenever trace amounts of V_2O_5 is dissolved in V_0 it coordinates with the ligand field oxides anions resulting the formation of Molecular Orbitals (MOs), which varies the electron density involved in the inner shells.

The Optical absorption bands taken from an extrapolation of the linear portion of the curves of Figure 3.4, 3.5, 3.6 gives direct, indirect and Urbach energy gap and is shown in Table 3.4. The values of direct, indirect band gap decreases from V_1 to V_5 glass samples. The Urbach energy value is increased from 0.2509 to 0.2946 eV up to 1.0 mol% of V_2O_5. The observed decrease in the optical band gap (Table 3.4.) with increase in the concentration of V_2O_5 up to 1.0 mol%, is due to the gradual increase in the concentration of VO^{2+} and VO^{+} ions, causes a creation of large number of donor centers; subsequently, the excited states of localized electrons originally trapped on V^{4+} and V^{3+} sites begin to overlap with the empty 3d states on the neighboring V^{5+} sites. As a result, the impurity band becomes more extended into the main band gap. This development might have shifted the absorption edge to the lower energy (Table 3.4.) which leads up to a significant shrinkage in the band gap. Hence it suggests that it has conducting or semiconducting nature of the glass.

IV. CONCLUSION

From this study, the following conclusions were drawn:

1. Density values of the samples are found to decrease from V_0-V_5 with the concentration of V_2O_5.

2. Average molecular weight (M), Inter ionic distance (r_i) and Polaron radius (r_p) values are found to decrease continuously with the concentration of V_2O_5.

3. Amorphous nature of the undoped and V_2O_5 doped KNZB sample is confirmed by the broad bands in XRD studies.

4. Two absorption bands appeared around 600 nm, 823 nm in all the glass samples. The band position seems to be non-linear variation is due to the characteristic $^2B_{2g}\rightarrow{}^2E_g$ transitions of tetravalent vanadium VO^{2+} ions in tetragonally distorted octahedral sites.

5. The Optical band gaps of KNZB glass samples varies from 4.007 to 3.477eV for direct transition and from 3.986 to 3.428 eV for indirect transitions.

6. The Urbach energies varies from 0.2509 to 0.2946 eV.

7. FT-IR absorption spectra of V_2O_5 doped KNZB glasses shows BO_4 structural groups which indicates the tetrahedral borate groups. The bands at 535 cm^{-1} and 830-837 cm^{-1} are assigned to ZnO tetrahedron and the presence of V_2O_5.

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