

Spectroscopic Investigation on Zinc Oxy Fluoro Borate Glasses Doped with V₂O₅

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Abstract - In this work, glass systems of the composition (10-x) ZnO-30ZnF₂-60B₂O₃: xV₂O₅ where (x = 0.2, 0.4, 0.6, 0.8, 1.0 mol %) have been prepared by the conventional melt quenching technique. Optical absorption, IR and ESR of these glass samples has been investigated. Optical absorption spectra exhibits two broad absorption bands at about 640 and 1020 nm due to ²B₂→²B₁ and ²B₂→²E transitions of VO²⁺ ions. With increase in the concentration of V₂O₅, the intensity of these peaks is observed to increase with a red shift. The IR spectral studies indicated that the glass samples contain various structural units with the linkages of the type B-O-B, V-O-V; the increasing content of V₂O₅ in the glass samples seemed to have weakened such linkages. The ESR results indicate that the ratio $\Delta g_{\parallel} / \Delta g_{\perp}$ is observed to decrease gradually with concentration of V₂O₅. Finally, the analysis of the results of OA, ESR spectra of the studied glass has indicated that a considerable proportion of vanadium ions do exist in V⁴⁺ state in addition to V⁵⁺ state with an increase in the concentration of V₂O₅.

Key Words: Glasses, OA, IR, ESR.

I. INTRODUCTION

The borate glasses containing ZnO have found many technological applications in gas sensors, catalysts, solar cells, display panels etc., due to high in thermal conductivity, low in specific heat, soaring in insulating strength, low in thermal expansion coefficient and good transparency [1-4]. By adding ZnF₂ to ZnO-B₂O₃ glasses, it is expected to lower the viscosity and liquidus temperature to a considerable extent and also widens the glass-forming region of the system [5-7].

A vanadium doped glasses are potential candidates in technological applications such as in electrical threshold, optical and memory switching devices, cathode materials for solid, devices and optical fiber [8-16] due their superior properties such as relatively high electrical conductivity, good semi conducting properties, chemical durability, low crystallization tendency and melting point [17-23]. V₂O₅ is a conditional glass former i.e., it readily forms glass with other glass formers or with modifiers such as alkali,

alkaline earth and transition metal oxides but it does not form glass on their own [24-27].

In a borate glass matrix, vanadium ions are easily dissolved due to some of the infrared vibrational bands of the structural groups of the vanadium ions and the BO₃ and BO₄ structural units are lying in the same region. The vanadium ions in the borate glass matrix can adopt two valence states, V⁴⁺ and V⁵⁺. The electrical conductivity of the material is expected to influence by the presence of the vanadium ions due to polaron hopping between valence states V⁴⁺ ↔ V⁵⁺. There are available several polaron hopping models to describe the conduction mechanism of vanadate glasses [28-30].

The aim of the present work is to synthesize ZnO-ZnF₂-B₂O₃ glasses doped with different concentration of V₂O₅ and investigate the structural changes due to the varied oxidation states of vanadium ion using optical absorption, IR and ESR spectral studies.

II. EXPERIMENTAL METHODS

A. Preparation of glasses

Zinc oxy fluoro borate glasses doped with different concentration of V₂O₅ are prepared by using analytic grade chemicals of ZnO, ZnF₂, H₃BO₃ and V₂O₅ as starting materials with 99.9% purity. The ratio of composition for the present study is mentioned in Table 1. These compounds in appropriate amounts (all in mol%) were mixed thoroughly in an agate motor and melted in an electric furnace in silica crucible around 950 °C for nearly 1 hour till a bubble free liquid is formed. The melt is then quenched at room temperature in air to form glass. The glasses so formed are annealed at 250 °C in another furnace and cooled to room temperature at the rate of about 1°C per minute to relieve the structural stress.

B. MEASUREMENTS

The X-ray diffraction patterns of the samples in the powder state are recorded on Xpert PRO, analytical X-ray diffractometer. The Differential Scanning Colorimetric (DSC) traces for the present samples are recorded on universal V24.2 Build 107 differential scanning calorimeter with programmed heating rate of 10 °C /min in the temperature range 30-900 °C. The optical absorption spectra of well polished V₂O₅ doped glass samples are recorded on Model V-670 UV-vis-NIR spectrophotometer in the wavelength region of 300-2100 nm. The IR transmission spectra of the present samples are recorded on a JASCO-FT/IR-5300 spectrophotometer in the spectral region 400-2000 cm⁻¹ using KBr pellets containing pulverized sample, which are pressed in a vacuum die at -680 MPa. The ESR spectra of the samples in the powder form are recorded on JEOL JES-TE5100 X-band EPR spectrometer at room temperature.

Table 1: Composition of glasses for the present study

Glass Sample	Glass composition
V ₀	10.0ZnO-30ZnF ₂ -60B ₂ O ₃
V ₂	9.8ZnO-30ZnF ₂ -60B ₂ O ₃ -0.2V ₂ O ₅
V ₄	9.6ZnO-30ZnF ₂ -60B ₂ O ₃ - 0.4V ₂ O ₅
V ₆	9.4ZnO-30ZnF ₂ -60B ₂ O ₃ - 0.6V ₂ O ₅
V ₈	9.2ZnO-30ZnF ₂ -60B ₂ O ₃ - 0.8V ₂ O ₅
V ₁₀	9.0ZnO-30ZnF ₂ -60B ₂ O ₃ -1.0V ₂ O ₅

Table 2 Physical Parameters of ZnO-ZnF₂-B₂O₃ glasses doped with different concentration of V₂O₅.

Sample	Density(g/cm ³)	Dopant ion conc. N _i (-10 ²⁰ ions/cm ³)	Inter ionic distance(Å)	Polaron radius(Å)	Refractive index(n)
V ₀	3.518	----	----	----	1.648
V ₂	3.512	0.52	1.24	0.50	1.645
V ₄	3.506	1.04	0.99	0.40	1.641
V ₆	3.501	1.55	0.86	0.35	1.637
V ₈	3.497	2.06	0.79	0.32	1.632
V ₁₀	3.492	2.56	0.73	0.29	1.628

Fig. 3 shows the optical absorption spectra of zinc oxy fluoro borate glasses doped with vanadium ions. For the pure glass sample V₀, the absorption edge observed at 330 nm. This absorption edge is found to be shifted gradually towards higher wavelength with an increase of the content of V₂O₅.

I. RESULTS

Physical parameters such as vanadium ion concentration N_i, mean vanadium ion separation R_i, polaron radius R_p for the present samples were evaluated from the measured values of the density and presented in Table 2. These observations clearly indicate that the density of the samples increases lightly with the concentration of vanadium ions.

Fig. 1 shows the XRD patterns of zinc oxy fluoro borate glasses doped with different concentrations of V₂O₅. These X-ray diffraction patterns confirm the amorphous nature in the samples.

Fig. 2 represents the DSC traces of the present studied glass samples recorded from 300 to 850 K. The traces have exhibited an endothermic effect due to glass transition temperature T_g followed by a distinct exothermic effect due to crystallization temperature T_c. The values of T_g and T_c acquired for the present studied glasses are furnished in Table 3. The value (T_c-T_g) is found to increase with the increase in the concentration of vanadium ions in the glass network, points out that the increasing resistance of the glass samples.

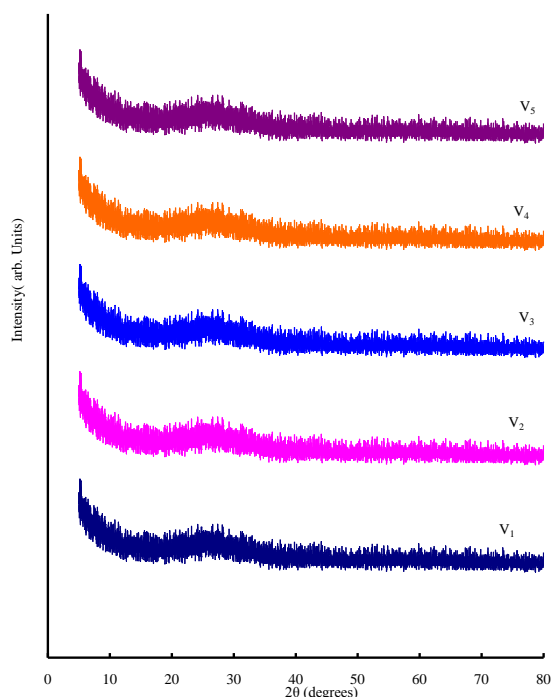


Fig. 1. XRD patterns of ZnO-ZnF₂-B₂O₃ glasses doped with different concentrations of V₂O₅

Additionally, the spectra of V₂ glass (doped with 0.2 mol % of V₂O₅) have exhibited two wide absorption bands at 640 and 1070 nm, in which these bands are attributed to ²B₂→²B₁ and ²B₂→²E transitions of VO²⁺ ions [31]; with an increase in the concentration of V₂O₅ up to 1.0 mol %, the half width and intensity of these bands are observed to increase and shifted slightly towards higher wavelength.

Table 3
 DSC data of ZnO-ZnF₂-B₂O₃: V₂O₅ glasses.

Sample	T _g (K)	T _c (K)	T _c -T _g
V ₂	651	720	69
V ₄	644	725	81
V ₆	638	732	94
V ₈	632	745	113
V ₁₀	628	768	140

Fig. 4 shows the Urbach plots of the present studied glasses. From these plots, the optical band gap is obtained by extrapolating the linear region of the curve to the hv axis. The obtained optical band along with cutoff wavelengths and band positions for the present glass samples are given Table 4. From this data, it is observed that the value of optical band gap E₀ is found to decrease with the increase in concentration of vanadium.

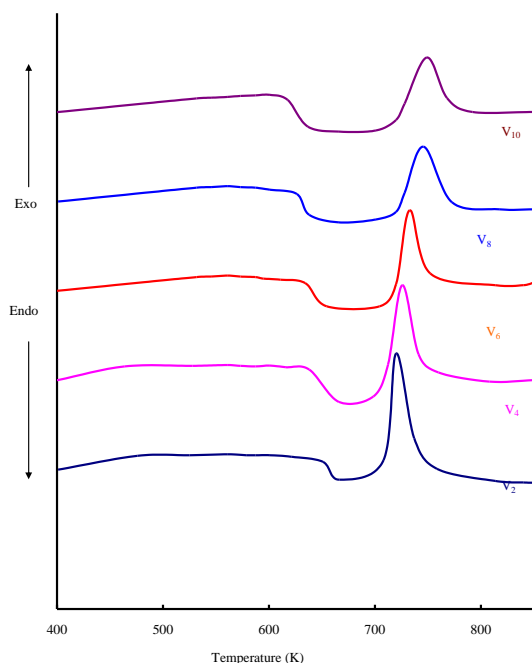


Fig. 2. DSC traces of ZnO-ZnF₂-B₂O₃ glasses doped with different concentrations of V₂O₅

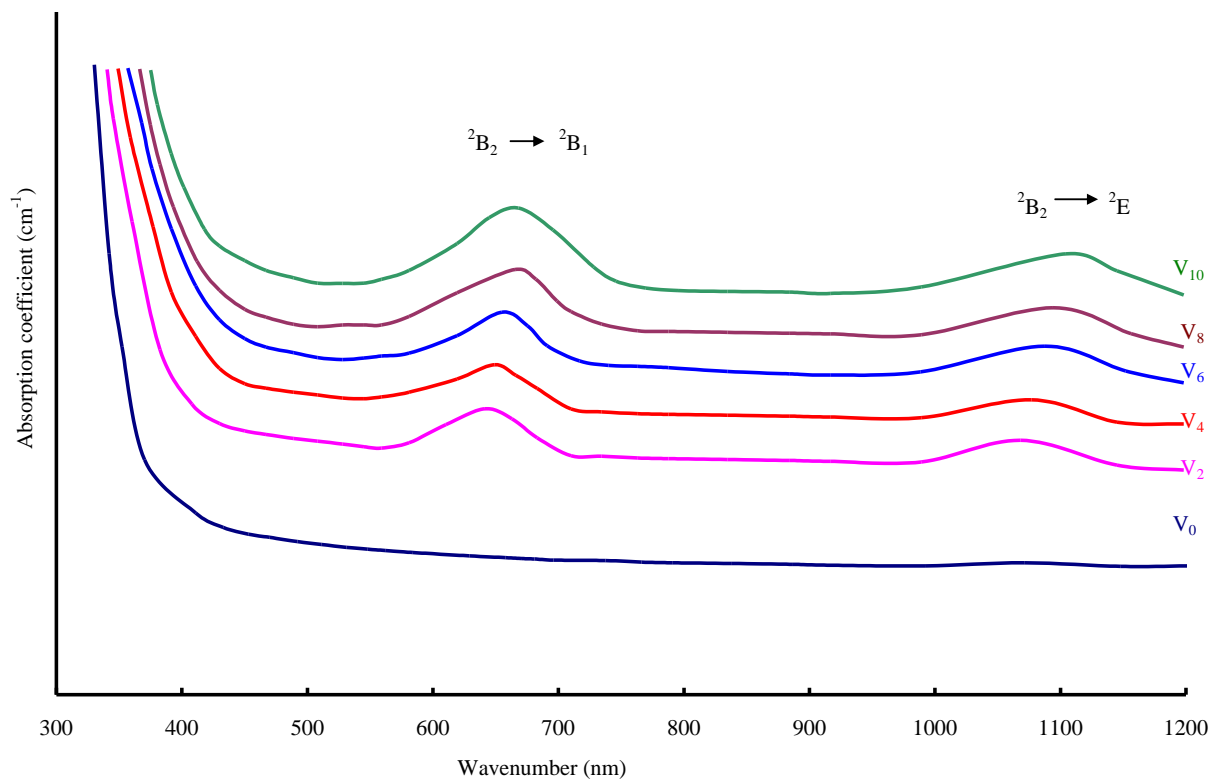


Fig. 3. Optical absorption spectrum of ZnO–ZnF₂–B₂O₃ glasses doped with different concentrations of V₂O₅.

Table 4
 Data on optical absorption spectra of ZnO–ZnF₂–B₂O₃: V₂O₅ glasses.

Sample	Cut-off wavelength (nm)	Optical band gap E _o (eV)	Position of ² B ₂ → ² B ₁ band (nm)	Position of ² B ₂ → ² E band (nm)
V ₀	330	2.72		
V ₂	340	2.58	642	1068
V ₄	351	2.48	649	1077
V ₆	357	2.41	655	1081
V ₈	366	2.36	665	1099
V ₁₀	375	2.29	668	1104

Fig. 5 shows the experimental FT-IR spectra of V₂O₅ doped Zinc oxy fluoro borate glasses.

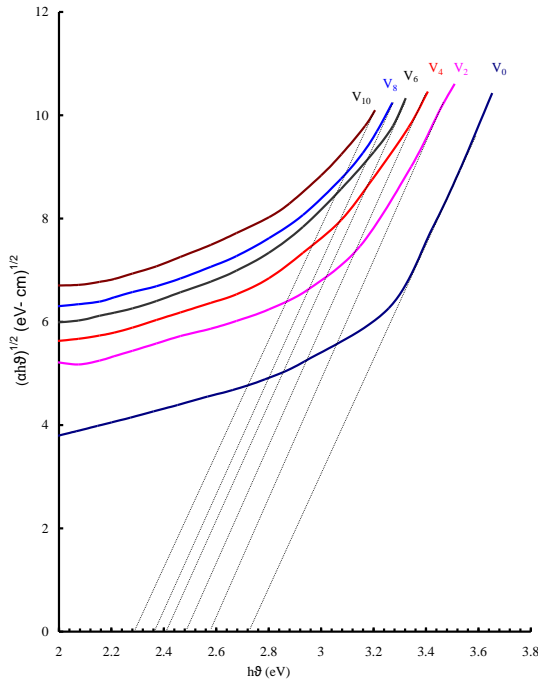


Fig. 4. Tauc plots of ZnO-ZnF₂-B₂O₃ glasses doped with different concentrations of V₂O₅.

The IR spectrum of V₂O₅ free ZnO-ZnF₂-B₂O₃ glass show the presence of the following bands at ~460, ~700, ~1026, ~1397 cm⁻¹. The band at ~460 cm⁻¹ was ascribed to the vibrations of ZnO₄ tetrahedral units [32–34]. At 700 cm⁻¹ appears a band due to the bending vibrations of B-O-B linkage in the borate network. Absorption from ~1026 cm⁻¹ can be due to B-O stretching vibrations in BO₄ units while the band at ~1397 cm⁻¹ was assigned to B-O stretching vibrations of in BO₃ units. The addition of V₂O₅ in the ZnO-ZnF₂-B₂O₃ glass matrix, ~600 cm⁻¹ appears a new band, which can be due to V-O-V bending vibrations. In the region of BO₄ units at about 1030 cm⁻¹ band due to vibrations of isolated VO groups in V₂O₅ trigonal bipyramids is also reported [35]. The intensity of BO₃ structural units is observed to increase, whereas that of the bands due to BO₄ is observed to decrease with a

gradual increasing in the content of V₂O₅ up to 1.0 mol %. The pertinent data related to FT-IR spectra of these glasses are given in Table 5.

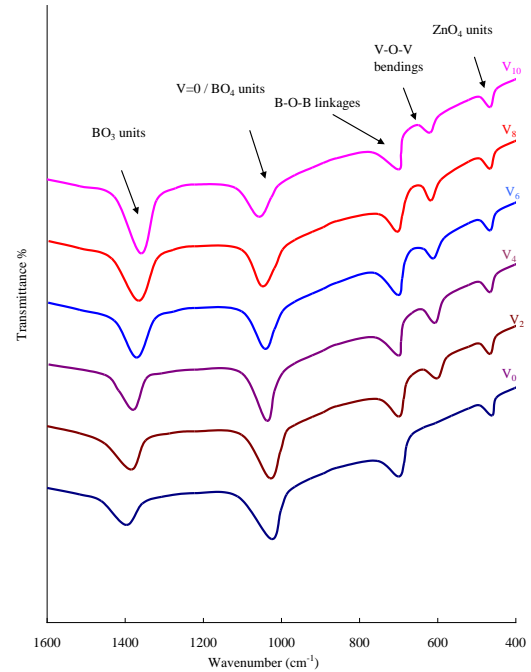


Fig. 5 IR spectrum of ZnO-ZnF₂-B₂O₃ glasses doped with different concentrations of V₂O₅.

The ESR spectra of zinc oxy fluoro borate glasses doped with different concentrations of V₂O₅ are presented in Fig. 6 recorded at room temperature. It is observed to be complex made up of resolving hyperfine components arising from unpaired (³d₁) electron with ⁵¹V isotope whose spin is 7/2 in an axially symmetric crystal field. From these spectra, g_{||} and g_⊥ values are evaluated and presented in Table 6. From this data, this is observed that an increasing degree of resolution and the intensity of signal with the increased content of V₂O₅.

Table 5

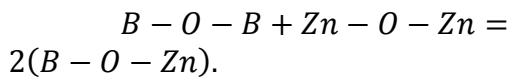
Data on various band positions (cm⁻¹) of IR spectra of ZnO-ZnF₂-B₂O₃: V₂O₅ glasses.

Sample	Borate groups			ZnO ₄	V-O-V units
	BO ₃	V=O/BO ₄	B-O-B		
V ₀	1397	1026	701	460	
V ₂	1384	1030	700	462	600
V ₄	1377	1036	700	464	606
V ₆	1370	1044	704	460	610
V ₈	1365	1051	700	458	614
V ₁₀	1358	1059	701	460	621

II. DISCUSSION

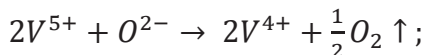
B₂O₃ is a well-known strong glass former oxide, the structure of vitreous B₂O₃ is composed essentially of BO₃ triangles forming three-member boroxol rings connected by B-O-B linkages. Moreover, the addition of a modifier oxide causes a progressive change of BO₃ triangles to BO₄ tetrahedra and results in the formation of various cyclic units like diborate, triborate, tetraborate or pentaborate groups.

ZnO can exist either as in octahedral modifying positions or as a network forming ZnO₄ tetrahedral. When glass modifier ZnO enters the glass, network break the B-O-B, Zn-O-Zn bonds and form easily B-O-Zn bridges, this can be related to the reaction



The B-O-Zn linkages is more stable relative to the mixture of B-O-B and Zn-O-Zn linkages [36, 37] and introduces co-ordinated defects known as dangling bonds along with non-bridging oxygen ions; in this case Zn²⁺ is octahedrally co-ordinated. However, ZnO may also participate in the glass network with ZnO₄ structural units when zinc is linked to four oxygen ions in a covalency bond configuration.

Vanadium ions are expected to be present mainly in V⁵⁺ states in the Zinc oxy fluoro borate glass matrix. However, there is a chance to exist in V⁴⁺ state with the following redox equilibrium during the melting of the glasses at higher temperatures:



The V⁵⁺ ions take part network forming positions with VO⁵ structural units where as V⁴⁺ ions may distort the glass network.

The optical absorption spectrum of vanadium doped glass has exhibited two wide absorption bands at 640 and 1070 nm. The bands are attributed due to ²B₂ → ²B₁ and ²B₂ → ²E_g transitions of 3d¹ electron in the V⁴⁺ state; the assignment of these bands has been made on the basis of an energy level scheme for molecular orbitals of VO²⁺ ion in a ligand field of C_{4v} symmetry provided by Bullhausen and Gray [31]. The half width and peak height of these bands are observed to increase and shifted slightly towards

higher wavelength with increase in the concentration of V₂O₅ up to 1.0 mol%. V⁴⁺ ion belongs to d¹ configuration with ²D as the ground state. In the presence of pure octahedral crystal field, the ²D state splits into ²T₂ and ²E, while an octahedral field with tetragonal distortion further splits the ²T₂ level into ²E and ²B₂; among these, the ²B₂ will be the ground state. Further ²E level splits into ²A₁ |3z² - r²> and ²B₁ |x² - y²> where as ²B₂ splits into three |xy>, |yz> and |zx> states. Thus, for the Vanadyl ions we can expect 3 bands corresponding to the transitions ²B₂ → ²B₁ (d_{xy} → d_{x²-y²}), ²B₂ → ²E (d_{xy} → d_{zx,yz}) and ²B₂ → ²A₁ (d_{xy} → d_{z²}). However, in the spectra of the present glasses, only the first two bands are observed.

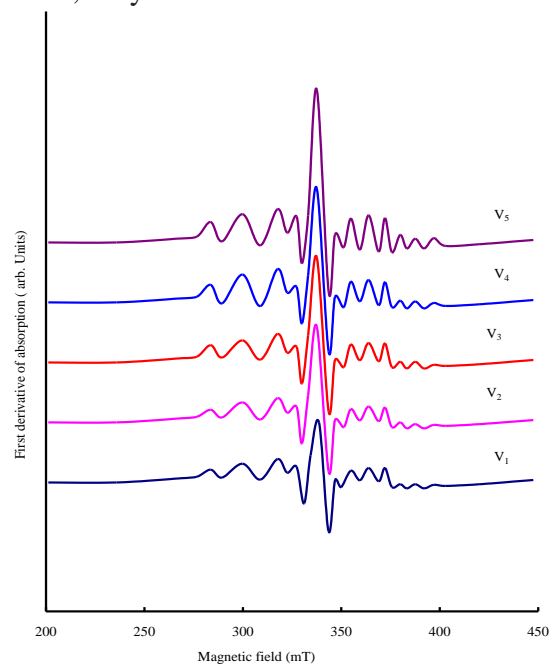


Fig. 6. ESR spectrum of ZnO-ZnF₂-B₂O₃ glasses doped with different concentrations of V₂O₅.

We can understand the observed decrease in the optical band gap with an increase in the concentration of V₂O₅ is as follows: The gradual increase in the concentration of Vanadyl ions, causes a creation of a large number of donor centers; subsequently, the excited states of localized electrons originally trapped on VO²⁺ sites begin to overlap with the empty 3d states on the neighboring V⁵⁺ 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 which leads up to a significant contraction in the band gap.

From the IR spectra, it is noticed that with the gradual increase in the concentration of V_2O_5 , the intensity of BO_3 structural units is observed to increase, whereas that of the band due to BO_4 structural units is decreased. Such observation clearly indicates an increase in the concentration of Vanadyl ions that induce structural disorder in the glass network.

The ESR spectra of the present studied glass samples consist of the well-resolved hyperfine structure with eight components of the electron-nuclear interactions corresponding to eight values of nuclear magnetic quantum numbers: $M_I = -7/2, -5/2, \dots, +7/2$ in accordance with selection rules $\Delta M_I = 0$ and $\Delta M_S = \pm 1$. The variation of ESR line width and the resolution with the concentration of V_2O_5 is

obviously due to the variation in the concentration of V^{4+} ions and also due to structural and microstructural modifications, that can produce fluctuations of the degree of distortion or even of the coordination geometry of V^{4+} sites. The observed broadening of the ESR signal with the concentration of V_2O_5 indicates the growing presence of V^{4+} ions [38]. The quantitative analysis of ESR results indicates that the ratio $\Delta g_{\parallel} / \Delta g_{\perp}$ is observed to decrease (Table 6) gradually with a concentration of V_2O_5 , indicating an increasing degree of distortion (elongation) of the VO_6 octahedron.

Table 6
Data on ESR spectra of $ZnO-ZnF_2-B_2O_3: V_2O_5$ glasses.

Sample	g	g_{\perp}	Δg	Δg_{\perp}	$\Delta g / \Delta g_{\perp}$
V ₂	1.837	1.940	0.159	0.060	2.656
V ₄	1.833	1.937	0.164	0.062	2.645
V ₆	1.829	1.935	0.166	0.065	2.554
V ₈	1.827	1.934	0.168	0.066	2.545
V ₁₀	1.824	1.932	0.169	0.068	2.485

III. CONCLUSIONS

Zinc oxy fluoro borate glasses doped with different concentration of V_2O_5 have been investigated. The DSC studies have indicated that the glass forming ability increases with an increase in the concentration of V_2O_5 . The IR spectral studies indicated that the glass samples contain various structural units with the linkages of the type B–O–B, V–O–V; the increasing content of V_2O_5 in the glass samples seemed to have weakened such linkages. The Optical absorption and ESR studies have indicated that a considerable proportion of vanadium ions do exist in V^{4+} state in addition to V^{5+} state with an increase in the concentration of V_2O_5 .

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