

# SPECTROSCOPIC STUDIES OF VANADIUM DOPED LEAD ANTIMONY BORATE GLASSES

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## ABSTRACT

Glasses with the composition  $30 \text{PbO} - 25 \text{Sb}_2\text{O}_3 - (45-x) \text{B}_2\text{O}_3 - x \text{V}_2\text{O}_5$  for  $x = 0$  to  $1$  were prepared in steps of  $0.2$  by the melt-quenching method. Various physical parameters, viz., density, molar volume, and oxygen packing density, were evaluated. The samples were characterized by X-ray diffraction and differential scanning calorimetric techniques. XRD, DSC, FTIR spectra, optical absorption and ESR spectra at room temperature have been investigated. Oxide ion polarizability of all the samples was calculated according to Dimmitrov –Sakka relation. Optical basicity calculation of all the samples was done with the help of J.Duffy equation. Electronic polarizabilities were calculated using Lorentz -Lorentz equation. The variations observed in all these properties due to different concentration of  $\text{V}_2\text{O}_5$  have been analyzed.

**Index Terms:** *Electronic polarizability, ESR Studies, FTIR Spectra, DSC curves. Optical basicity, Optical absorption, PbO-Sb<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> glasses,*

## I. INTRODUCTION

Heavy metal oxide glasses like PbO-Sb<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> glasses have gained importance in recent years due to their non-linear optical susceptibility ( $\chi^3$ ) [1] and maximum phonon energy. Emission quantum efficiency from a given level strongly depends upon the phonon energy of the host medium. Non radiative loss to the lattice is small and the fluorescence quantum efficiency is high in heavy metal oxide glasses [2]. These properties makes them suitable for many applications in various technological fields such as ultrafast optical triggers, optically poled materials, power limiters and broad band optical amplifiers operating around  $1.5 \mu\text{m}$  [3-8].

Glasses containing vanadium ions have attracted much interest in solid-state chemistry and materials science in recent years, since  $\text{V}_2\text{O}_5$  is known to participate in the glass network with  $\text{VO}_5$  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 [18]. Several vanadate glasses show semiconducting behaviour with the electrical conductivity of  $10^{-3}$  to  $10^{-5} (\Omega \text{cm})^{-1}$ , which is known to be due to the electron hopping between  $\text{V}^{4+}$  and  $\text{V}^{5+}$  ions existing in the glass network, and are identified as n-type semiconductors for low values of the  $\text{V}^{4+}/\text{V}^{5+}$  ratio [19]. The vanadium ions may also exist in the glass network in  $\text{V}^{2+}$  and  $\text{V}^{3+}$  states [19]. 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 PbO-Sb<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> glass network, because some of the infrared vibrational 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.

Electronic polarizability of material is closely related to the field of optics and electronics. Optical non-linearity is caused by electronic polarization of material when exposed to intense light beams. Hence the nonlinear response of the material is governed by electronic polarizability [12].

The present investigation was undertaken to obtain a comprehensive understanding of the influence of vanadium ions on electronic polarizability, optical basicity, optical absorption and ESR studies. The structural probing of vanadium ions by these studies especially in heavy metal oxide-based glass like lead antimony oxide, is highly desirable for considering these materials for the practical applications in nonlinear optical devices mentioned above.

## II. EXPERIMENTAL METHODS

For the present study, glasses of composition  $30 \text{ PbO} - 25 \text{ Sb}_2\text{O}_3 - (45 - x) \text{ B}_2\text{O}_3 - x \text{ V}_2\text{O}_5$  with  $x = 0, 0.2, 0.4, 0.6, 0.8$  and  $1.0$  are chosen and samples are labeled as V0, V2, V4, V6, V8 and V10 respectively. Appropriate amounts of AR grade reagents of PbO,  $\text{Sb}_2\text{O}_3$ ,  $\text{H}_3\text{BO}_3$  and  $\text{V}_2\text{O}_5$  powders are thoroughly mixed in agate mortar and melted in a silica crucible in the temperature range of 900 to 950 °C in a programmable electrical furnace for thirty minutes until bubble free liquid is formed. The resultant melt is poured in a brass mold and subsequently annealed at 250 °C for 2 hours. The samples prepared were then ground and optical polished to the dimensions of  $1 \text{ cm} \times 1 \text{ cm} \times 0.2 \text{ cm}$ . The density  $d$  of the glasses was determined by the standard Archimedes' principle of using *o*-xylene (99.99% pure) as the buoyant liquid. Refractive index ( $n_d$ ) of the samples was measured (at  $\lambda=589.3 \text{ nm}$ ) using an Abbe refractometer with mono bromo naphthalene as the contact layer between the glass and the refractometer prism. The X-ray diffractograms of all the samples were recorded on Rigaku diffractometer mini flex with Cu-K $\alpha$  radiation. The glass transition temperatures of these glasses were determined by differential scanning calorimetry traces that were recorded using DSC Q20 (TA-Instruments). The heating rate was maintained as 10 °C/min and the values of  $T_g$  (glass transition temperature) were evaluated to an accuracy of  $\pm 1.0$  °C. The FTIR transmission spectra of these glasses were recorded using a Perkin Elmer Spectrometer in the spectral range 400–4000  $\text{cm}^{-1}$ . The optical absorption spectra of the samples were recorded at room temperature in the spectral wavelength range covering 300–1300 nm with a spectral resolution of 1 nm using JASCO Model V-670 UV-VIS-NIR spectrophotometer. Electron spin resonance (ESR) spectra of powder samples of all compositions were recorded at room temperature using X-Band JEOL JESTE 100 spectrometer in the frequency range of 8.8–9.6 GHz.

## III. RESULTS AND DISCUSSION

From the measured values of the density and average molecular weight of the samples, various other physical parameters such as molar volume  $V_m$ , oxygen packing density  $O$ ,  $\text{V}^{5+}$  ions concentration  $N_i$ , mean  $\text{V}^{5+}$  ions separation  $r_i$ , polaron radius  $r_p$  in  $\text{PbO-Sb}_2\text{O}_3\text{-B}_2\text{O}_3:\text{V}_2\text{O}_5$  glass samples are computed using standard equations [13]. Using the refractive index, various other optical parameters viz., molar refractivity ( $R_M$ ), electronic polarizability ( $\alpha_e$ ) have also been evaluated. As the concentration of  $\text{V}^{5+}$  ions increased, a considerable increase in the density or a considerable decrease in the molar volume of samples is observed. Modification of the geometrical configurations of the glass network, change in coordination and the variation of dimensions of the

interstitial holes can be considered to be responsible for such a variation of density. The oxygen packing density is also found to increase with the increase in the concentration of  $V^{5+}$  ions (Fig.1). Such an increase indicates an increase in the structural compactness of the samples. The specific refraction gives the average molar refraction of the samples and calculated using Lorentz-Lorentz equation [14-15].

$$R_m = \left( \frac{n^2 - 1}{n^2 + 2} \right) V_m \tag{1}$$

where  $V_m$  is molar volume and  $n$  is the refractive index.

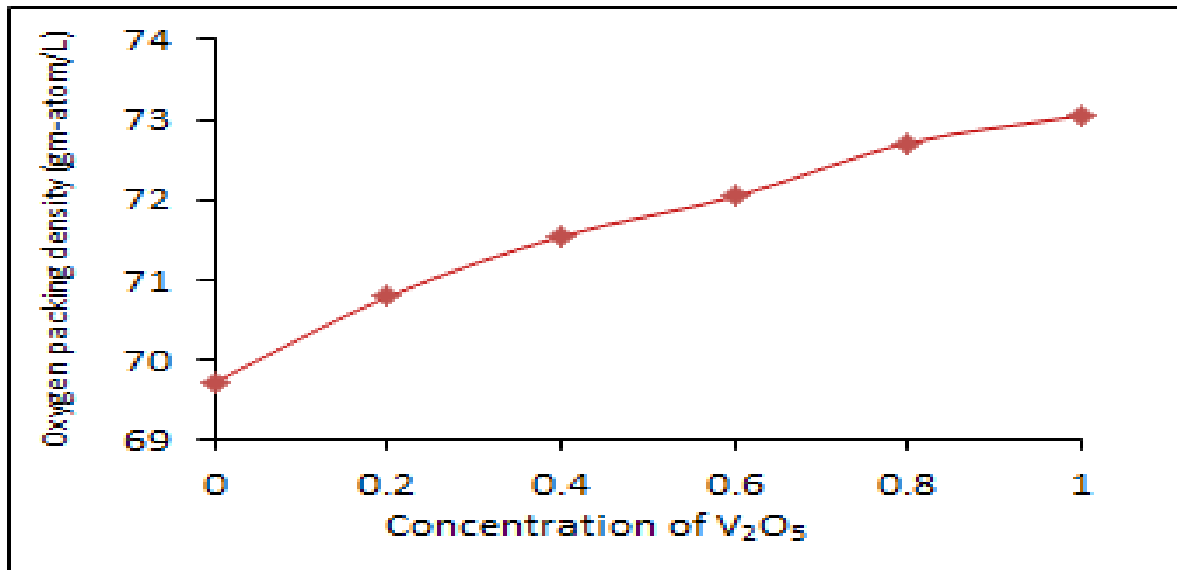


Fig. 1. Variation of oxygen packing density of  $PbO-Sb_2O_3-B_2O_3$  glasses with the concentration of  $V_2O_5$ .

The Lorentz-Lorentz equation presents the polarizability, i.e., the magnitude of response of the electrons to an electromagnetic field [16]. When the material is exposed to intense light beams, the electronic polarization causes the optical non linearity. When Avogadro number  $N_A$  is introduced, the Lorentz –Lorentz equation can be written as

$$R_m = \left( \frac{n^2 - 1}{n^2 + 2} \right) V_m = \frac{4}{3} \pi N_A \alpha_e \tag{2}$$

where  $\alpha_m$  is the molar electronic polarizability in  $\text{\AA}^3$  and  $R_m$  is molar refraction in  $\text{cm}^3$ .

Rearranging the terms, we can write electronic polarizability

$$\alpha_e = \left( \frac{3}{4\pi} \right) \left( \frac{R_M}{N_A} \right) \tag{3}$$

The relationship between oxide ion polarizability  $\alpha_{O^{2-}} (E_{opt})$  and  $E_{opt}$  is given by Dimitrov and Sakka [17] relation.

This equation is modified by Banu [18] and Vittal [19] and applicable for many glasses. The relationship is given by

$$\alpha_{O^{2-}}(E_{opt}) = \left[ \frac{V_m}{2.52} \left( 1 - \frac{(E_{opt})^{1/2} - 0.98}{1.23} \right) - \sum_i p\alpha_i \right] q^{-1} \quad (4)$$

The optical basicity of an oxide glass defines the ability of the glass to donate negative charge to the probe ion. It represents the electronic state of the oxide species in a way similar to how it is represented by electronic polarizability. The optical basicity is calculated from the values of oxide ion polarizability (suggested by Duffy [20]) from the following equation.

$$\Lambda(E_{opt}) = 1.67 \left[ 1 - \frac{1}{\alpha_{O^{2-}}(E_{opt})} \right] \quad (5)$$

Various physical parameters of PbO-Sb<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> glasses doped with vanadium ions were presented in

**Table 1.**

Table 1. Physical parameters of PbO-Sb<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> glasses doped with vanadium ions.

Physical Parameters	Glass					
	V0	V2	V4	V6	V8	V10
1 Average MW (g/mol)	171.1	171.3	171.6	171.8	172.06	172.29
2 Density, ρ (g/cc) (±0.001)	4.972	5.047	5.098	5.133	5.178	5.201
3 Molar Volume, V <sub>m</sub> (MW/ρ) (±0.01)	34.42	33.96	33.66	33.48	33.23	33.13
4 Oxygen mol % , O (±0.001)	2.4	2.404	2.408	2.412	2.416	2.42
5 Oxygen packing density (gm atom/L) (±0.01)	69.73	70.79	71.54	72.04	72.71	73.05
6 V <sup>5+</sup> ion concentration N(x10 <sup>21</sup> /cc) (±0.01)	0	17.74	35.79	53.97	72.5	90.9
7 Inter ionic distance, r <sub>i</sub> (Å) (±0.001)	-	3.83	3.03	2.65	2.41	2.22
8 Refractive index, n (±0.001)	1.504	1.515	1.522	1.529	1.535	1.539
9 Molar Refraction (R <sub>m</sub> ) (±0.001)	10.192	10.24	10.27	10.33	10.35	10.38
10 Polarizability (α <sub>e</sub> )(x10 <sup>-24</sup> ) (cm <sup>3</sup> )	4.042	4.057	4.069	4.093	4.101	4.113
11 Oxide ion polarizability α <sub>O<sup>2-</sup></sub> (E <sub>opt</sub> ) Å	7.612	10.641	11.518	11.997	12.411	12.689
12 Optical basicity, Λ(E <sub>opt</sub> )	1.451	1.513	1.525	1.531	1.535	1.538

The X-ray diffractograms of all the samples are presented in Fig. 2. The absence of sharp peaks in the X-ray diffraction pattern indicates the amorphous (glass) nature of the samples.

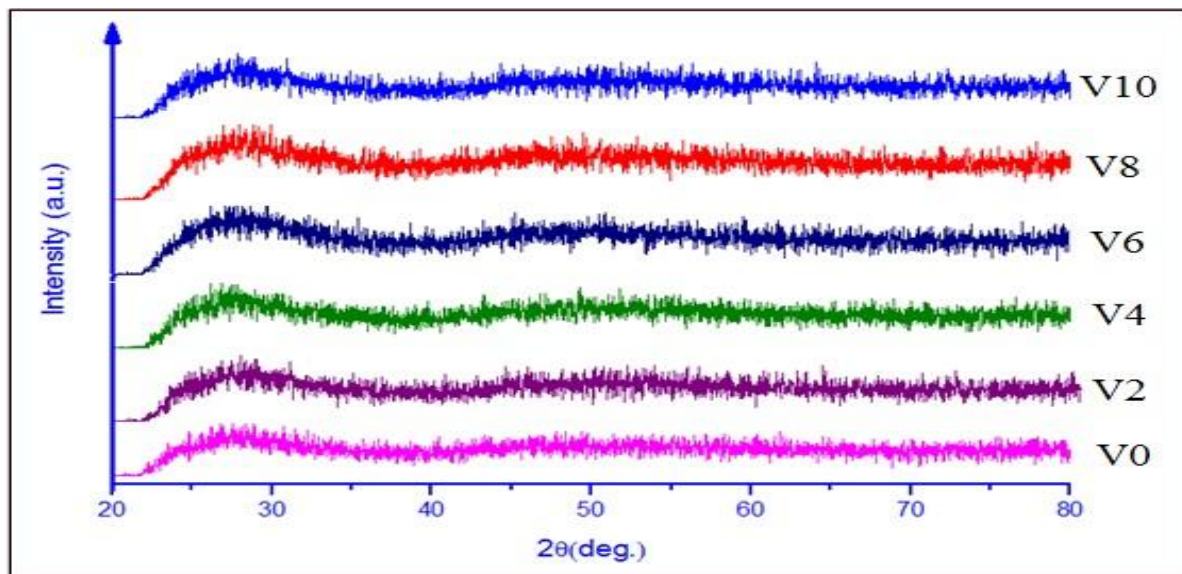
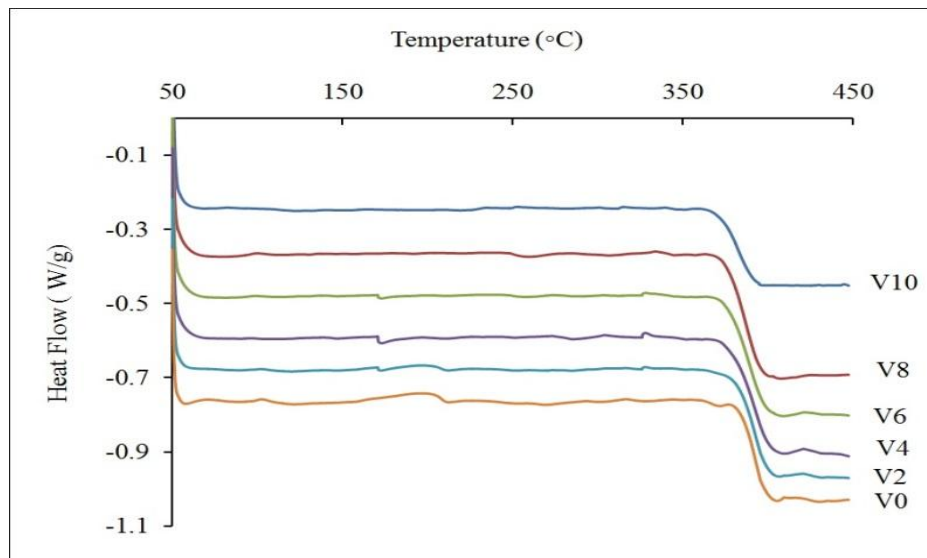


Fig. 2. X- ray diffractograms of PbO-Sb<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>:V<sub>2</sub>O<sub>5</sub> glasses.

The glass transition temperatures ( $T_g$ ) of all the glasses were presented in the Fig. 3. The DSC traces indicate typical glass transitions with the inflection points between 384 °C to 389 °C. Although the inflection points of all the samples appear to be nearly same, it is interesting that the glass transition temperature shows increasing trend with increase in dopant concentration. The glass transition temperature  $T_g$  for all the samples were presented in **Table 2**.

**Table 2 Thermal parameters of PbO-Sb<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>:V<sub>2</sub>O<sub>5</sub> glasses.**

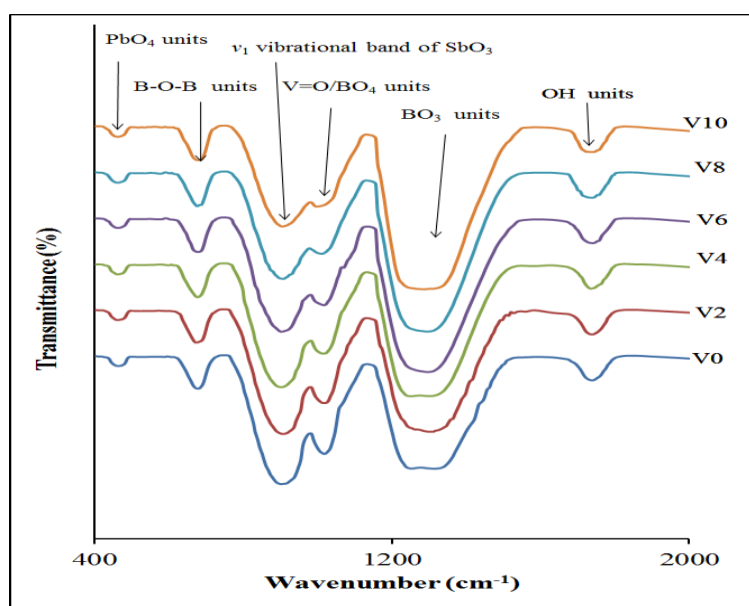
Glass	( $T_g$ ) °C
V0	384
V2	385
V4	386
V6	387
V8	388
V10	389



**Fig. 3. Variation of glass transition temperature of PbO-Sb<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> glasses with increasing in vanadium concentration.**

The FTIR spectra of vanadium doped LAB glasses were shown in the Fig .4. The spectra exhibits bands [21] at 462 cm<sup>-1</sup> due to PbO<sub>4</sub> units, at 692 cm<sup>-1</sup> due to bending vibrations of B-O-B units, at 923 cm<sup>-1</sup> due  $\nu_1$  vibrational band of SbO<sub>3</sub> ( $\nu_2$  and  $\nu_4$  bands seem to be missing), the band at 1022 cm<sup>-1</sup> is due to the vibrations of isolated V=O groups in the VO<sub>5</sub> trigonal bipyramids, at 1069 cm<sup>-1</sup> due to BO<sub>4</sub> units (merged with V=O bands) and at 1284 cm<sup>-1</sup> due to BO<sub>3</sub> bonds due to stretching vibrations in the tetrahedral BO<sub>3</sub> units in the borate network. The  $\nu_3$ -vibrational band seems to be merged with the band due to bending vibrations of B-O-B linkages and may have formed a common vibrational band due to B-O-Sb linkages.

With a gradual increase in the concentration of V<sub>2</sub>O<sub>5</sub>, the intensity of the band due to BO<sub>3</sub> units is increased where as that of the bands due to BO<sub>4</sub> and B-O-Sb structural units are decreased. Such observation clearly indicates an increase in the concentration of vanadyl ions that induce structural disorder in the glass network.



**Fig .4. FTIR spectra of PbO-Sb<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>:V<sub>2</sub>O<sub>5</sub> glasses.**



Visible absorption spectra of vanadium doped lead antimony borate glasses were shown in the Fig. 5. The optical absorption spectrum shows two broad absorption bands at 604 and 1045 nm. The spectral intensities of these bands are found to increase with the content of V<sub>2</sub>O<sub>5</sub>. A noticeable shift in the peak positions is also observed towards higher wavelength with increase in the concentration of V<sub>2</sub>O<sub>5</sub>. The bands are attributed to <sup>2</sup>B<sub>2g</sub>→<sup>2</sup>B<sub>1g</sub> (Δ⊥) and 2B<sub>2g</sub>→2E<sub>g</sub>(Δ||) transitions of 3d<sup>1</sup> electron in the V<sup>4+</sup> state. The assignment are made on the basis of energy level scheme for molecular orbitals of VO<sup>2+</sup> ion in a ligand field of C<sub>4v</sub> symmetry provided by Bull-Hausen and Gray [22]. The increase in intensity of these bands with mol% of vanadium ions indicates increase in concentration of VO<sup>2+</sup>.

The relation between the optical absorption coefficient α (ω) and optical band gap energy E<sub>opt</sub> is given by the equation [19]

$$\alpha(\omega) = \frac{\text{Const}(\hbar\omega - E_{\text{opt}})^2}{\hbar\omega} \tag{6}$$

This equation can be rearranged as

$$(\alpha\hbar\omega)^{1/2} = \text{Const} (\hbar\omega - E_{\text{opt}}) \tag{7}$$

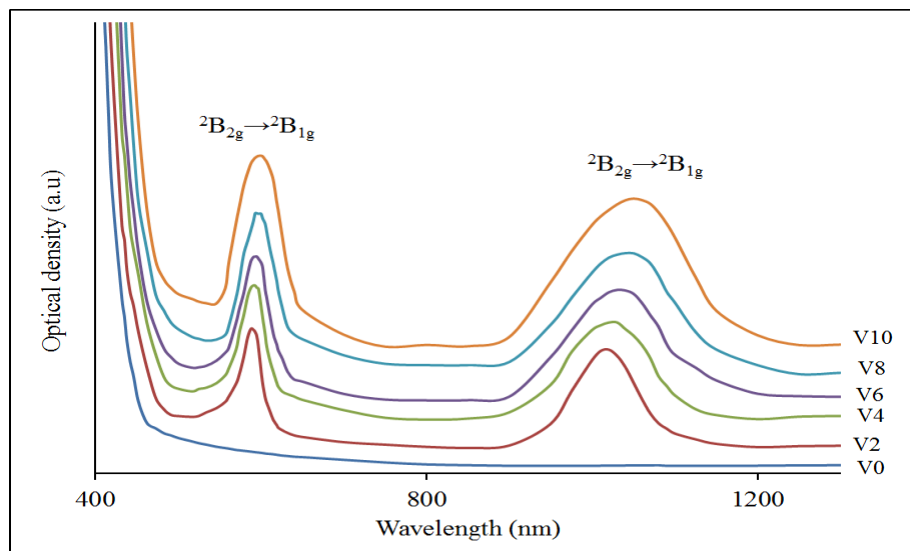


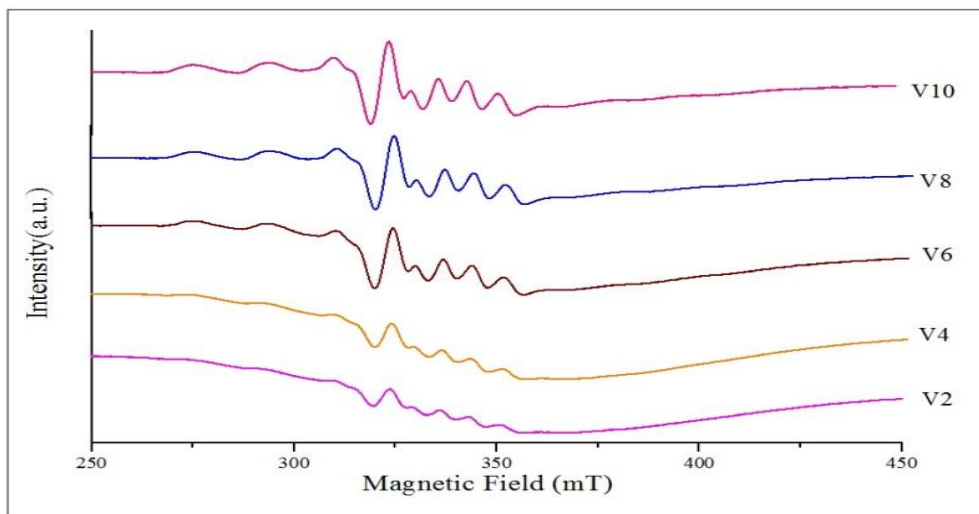
Fig. 5. Optical absorption spectra of PbO-Sb<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>:V<sub>2</sub>O<sub>5</sub> glasses recorded at room temperature.

Optical band gap for all the glasses were evaluated by drawing Tauc plots (Fig. 6) between (αħω)<sup>1/2</sup> and ħω using equation 7. The optical band gap is found to decrease gradually with increase the concentration of V<sub>2</sub>O<sub>5</sub>.

**Table 3. The optical parameters of PbO-Sb<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>:V<sub>2</sub>O<sub>5</sub> glasses.**

Name of the Sample	V0	V2	V4	V6	V8	V10
1 Cutoff Wavelength, λ(nm)(±1)	398	408	413	416	420	432
2 Optical Bandgap Energy, E <sub>opt</sub> (ev) (±0.001)	2.78	2.71	2.66	2.63	2.59	2.54
3 Urbach Energy, ΔE(eV) (±0.001)	0.511	0.527	0.534	0.541	0.549	0.568

The values of the Urbach energy (ΔE) were calculated by taking the reciprocal of slopes of the linear part in the lower photon energy region of the curve. The various optical parameters of vanadium doped lead antimony borate glasses are shown in **Table 3**.



**Fig. 6. ESR spectra of PbO-Sb<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>:V<sub>2</sub>O<sub>5</sub> glasses recorded at room temperature.**

Fig. 6 shows typical ESR spectra of lead antimony borate glasses doped with V<sub>2</sub>O<sub>5</sub>. ESR spectra is observed to be complex made up of resolved hyperfine components arising from unpaired 3d<sup>1</sup> electron [23] with <sup>51</sup>V isotope whose spin is 7/2. As the concentration of V<sub>2</sub>O<sub>5</sub> is increased, an increasing degree of resolution and intensity of the signal is observed. This is due to the increase in the concentration of V<sup>4+</sup> ions and also may be due to exchange couple between V<sup>3+</sup> ion and V<sup>4+</sup> ions [10]. The values of g<sub>||</sub>, g<sub>⊥</sub> and g<sub>||</sub>/g<sub>⊥</sub> are calculated for all the samples and furnished in **Table 4**. The spectra indicate that VO<sup>2+</sup> ions exist in the glass network in an octahedral site symmetry with tetragonal compression since g<sub>||</sub> ≤ g<sub>⊥</sub> ≤ g<sub>e</sub> [24].

Table 4. Summary of data on the ESR spectra of PbO-Sb<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>:V<sub>2</sub>O<sub>5</sub> glasses.

Glass	g <sub>  </sub>	g <sub>⊥</sub>	Δg <sub>  </sub> / Δg <sub>⊥</sub>
V2	1.925	1.931	1.097
V4	1.922	1.929	1.095
V6	1.919	1.926	1.092
V8	1.917	1.924	1.089
V10	1.914	1.921	1.086

The g<sub>||</sub>/g<sub>⊥</sub> ratio is observed to decrease gradually with increase in the concentration of V<sub>2</sub>O<sub>5</sub> which is an indication of increase in tetragonal distortion around vanadyl ions. The increase in the intensity of the signal with the concentration of V<sub>2</sub>O<sub>5</sub> indicates that there is an increase in the concentration of vanadyl ion complexes. These ions similar to conventional modifiers break the local symmetry and increase the degree of disorder in the glass network. Such increase of disorder is also reflected in the IR spectra. The increase in the intensity of the vibartional bands due to BO<sub>3</sub> structural units at the expense of BO<sub>4</sub> units, in fact supports this view point.

#### IV. CONCLUSIONS

The density of present glasses is increasing with increase in the mol% of V<sub>2</sub>O<sub>5</sub> almost linearly. The molar volume of the glass samples is decreasing where as the oxygen packing density is increasing with increase in in the vanadium ion concentration.



The increase in electronic polarizability with increase in the mol% of  $V_2O_5$  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 (0.43) whereas  $V_2O_5$  is an oxide with significant optical basicity (1.04). 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 cations. On the other hand lead antimony borate glasses doped with  $V_2O_5$  possess high optical basicity which means high donor ability of oxide ions [8].

The optical bandgap energy of the glasses is decreasing with increasing the concentration of vanadium ions whereas the Urbch energy and cut-off wavelength are increasing.

The FTIR spectra exhibited the bands due to  $PbO$ ,  $Sb_2O_3$ ,  $B_2O_3$  and  $V_2O_5$  functional groups in all the glasses investigated. The increase in the intensity of the band due to  $BO_3$  units and decrease in the intensity of  $BO_4$  and  $B-O-Sb$  structural units is observed with increase in  $V_2O_5$  concentration.

From the results of ESR and optical absorption spectra, it is clear that vanadium exist in two oxidation states, viz.,  $V^{5+}$  (non-magnetic) and  $V^{4+}$  (a paramagnetic  $3d^1$  ion) in the present glass matrices and the magnetic properties of these glasses obviously arise due to  $V^{4+}$  ion. The results of ESR spectra of glasses have indicated the highest covalent environment for 1 mol% of vanadium ions.

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