

Optical and ESR Studies of Lead Antimony Borate Glasses Doped with V_2O_5

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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. The samples were characterized by X-ray diffraction and differential scanning calorimetric techniques. Various physical parameters, viz., density, molar volume, and oxygen packing density, were evaluated. XRD, DSC, FTIR spectra, optical absorption and ESR spectra at room temperature have been investigated. The variations observed in all these properties due to different concentration of V_2O_5 have been analyzed. 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.

Index Terms— $\text{PbO-Sb}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses, Electronic polarizability, Optical basicity, ESR Studies, Optical absorption, FTIR Spectra, DSC curves.

1 Introduction

Heavy metal oxide glasses like $\text{PbO-Sb}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses have gained importance in recent years due to their non-linear optical susceptibility (χ^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 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 [18]. Several vanadate glasses show semiconducting behaviour with the electrical conductivity of 10^{-3} to 10^{-5} (Ωcm)⁻¹, 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 [19]. The vanadium ions may also exist in the glass network in V^{2+} and 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 $\text{PbO-Sb}_2\text{O}_3\text{-B}_2\text{O}_3$ 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.

2 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 , Sb_2O_3 , H_3BO_3 and V_2O_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 cm × 1 cm × 0.2 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 $\lambda=589.3$ 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 α 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 ± 1.0 °C. The FTIR transmission spectra of these glasses were recorded using a Perkin Elmer Spectrometer in the spectral range 400–4000 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.

3 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 , V^{5+} ions concentration N_i , mean 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 (α_e) have also been evaluated. As the concentration of 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].

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

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

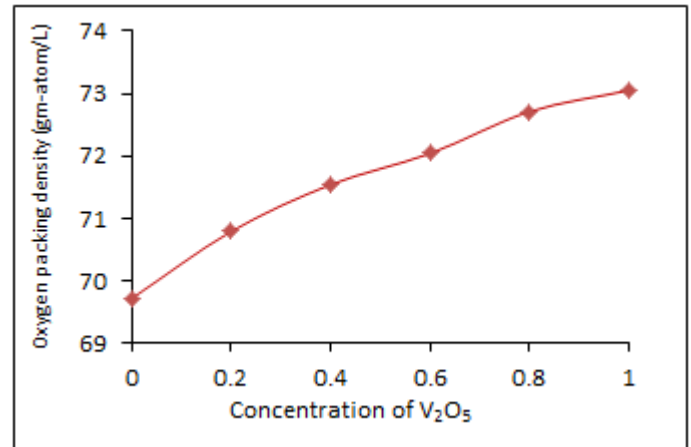


Fig. 1. Variation of oxygen packing density of $\text{PbO-Sb}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses with the concentration of V_2O_5 .

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

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

where α_m is the molar electronic polarizability in \AA^3 and R_m is molar refraction in cm^3 .

Rearranging the terms, we can write electronic polarizability

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

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-Sb₂O₃-B₂O₃ glasses doped with vanadium ions were presented in Table 1.

Table 1. Physical parameters of PbO-Sb₂O₃-B₂O₃ 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 _m (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 ⁵⁺ ion concentration N(x10 ²³ /cc) (±0.01)	0	17.74	35.79	53.97	72.5	90.9
7 Inter ionic distance, r _i (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 _m) (±0.001)	10.192	10.24	10.27	10.33	10.35	10.38
10 Polarizability (α _o)(x10 ⁻²⁴) (cm ³)	4.042	4.057	4.069	4.093	4.101	4.113
11 Oxide ion polarizability α _{o²⁻} (E _{opt}) Å	7.612	10.641	11.518	11.997	12.411	12.689
12 Optical basicity, Λ(E _{opt})	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.

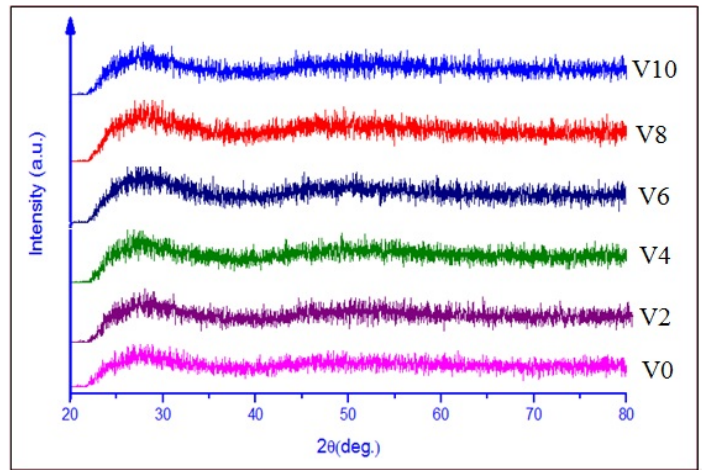


Fig. 2. X- ray diffractograms of PbO-Sb₂O₃-B₂O₃:V₂O₅ glasses.

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-Sb₂O₃-B₂O₃:V₂O₅ glasses.

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

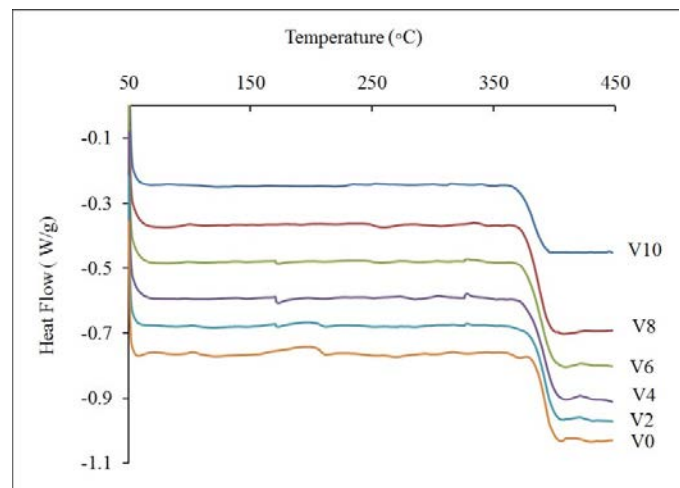


Fig. 3. Variation of glass transition temperature of PbO-Sb₂O₃-B₂O₃ glasses with increasing in vanadium concentration.

The FTIR spectra of vanadium doped LAB glasses were shown in the Fig. 4. The spectra exhibits bands [21] at 462 cm⁻¹ due to PbO₄ units, at 692 cm⁻¹ due to bending vibrations of B-O-B units, at 923 cm⁻¹ due to ν₁ vibrational band of SbO₃ (ν₂ and ν₄ bands seem to be missing), the band at 1022 cm⁻¹ is due to the vibrations of isolated V=O groups in the VO₅ trigonal bipyramids, at 1069 cm⁻¹ due to BO₄ units (merged with V=O bands) and at 1284 cm⁻¹ due to BO₃ bonds due to stretching vibrations in the tetrahedral BO₃ units in the borate network. The ν₃-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 V₂O₅, the intensity of the band due to BO₃ units is increased where as that of the bands due to BO₄ 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.

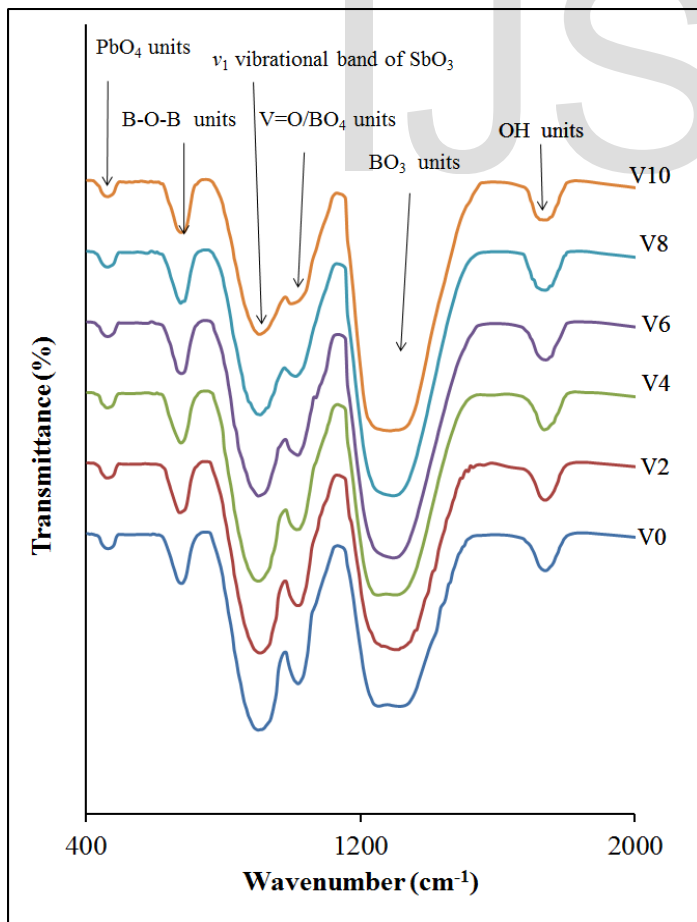


Fig. 4. FTIR spectra of PbO-Sb₂O₃-B₂O₃:V₂O₅ glasses.

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 V₂O₅. A noticeable shift in the peak positions is also observed towards higher wavelength with increase in the concentration of V₂O₅. The bands are attributed to ²B_{2g}→²B_{1g} (Δ₁) and 2B_{2g}→2E_g(Δ₁) transitions of 3d¹ electron in the V⁴⁺ state. The assignment are made on the basis of energy level scheme for molecular orbitals of VO²⁺ ion in a ligand field of C_{4v} 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 VO²⁺.

The relation between the optical absorption coefficient α(ω) and optical band gap energy E_{opt} is given by the equation [19]

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

This equation can be rearranged as

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

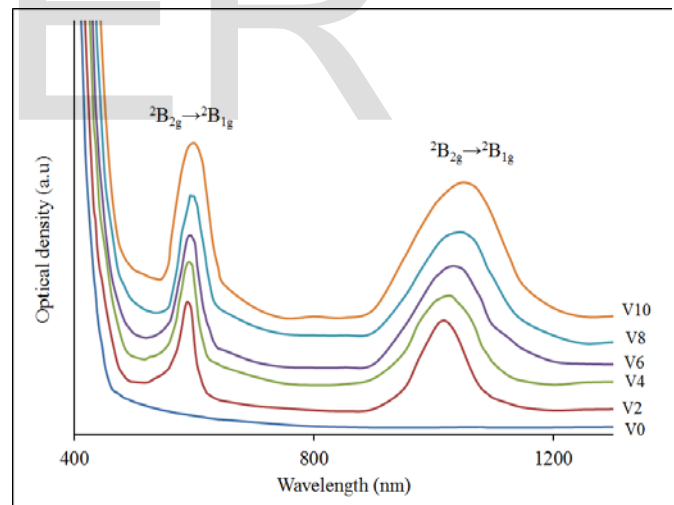


Fig. 5. Optical absorption spectra of PbO-Sb₂O₃-B₂O₃:V₂O₅ glasses recorded at room temperature.

Optical band gap for all the glasses were evaluated by drawing Tauc plots (Fig. 6) between (αħω)^{1/2} and ħω using equation 7. The optical band gap is found to decrease gradually with increase the concentration of V₂O₅.

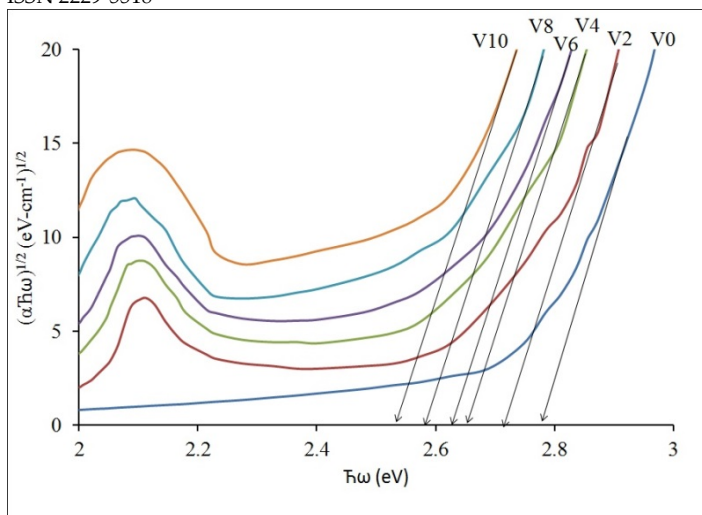


Fig.6 Urbach plots of PbO-Sb₂O₃-B₂O₃:V₂O₅ glasses

Table 3. The optical parameters of PbO-Sb₂O₃-B₂O₃:V₂O₅ 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 _{opt} (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. 7. ESR spectra of PbO-Sb₂O₃-B₂O₃:V₂O₅ glasses recorded at room temperature.

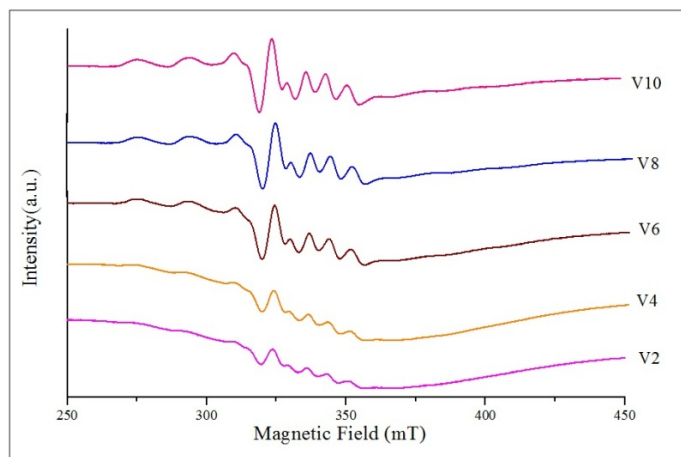


Fig. 7 shows typical ESR spectra of lead antimony borate glasses doped with V₂O₅. ESR spectra is observed to be complex made up of resolved hyperfine components arising from unpaired 3d¹ electron [23] with ⁵¹V isotope whose spin is 7/2. As the concentration of V₂O₅ is increased, an increasing degree of resolution and intensity of the signal is observed. This is due to the increase in the concentration of V⁴⁺ ions and also may be due to exchange couple between V³⁺ ion and V⁴⁺ ions [10]. The values of g_{||}, g_⊥ and g_{||}/g_⊥ are calculated for all the samples and furnished in Table 4. The spectra indicate that VO²⁺ ions exist in the glass network in an octahedral site symmetry with tetragonal compression since g_{||} ≤ g_⊥ ≤ g_e [24].

Table 4. Summary of data on the ESR spectra of PbO-Sb₂O₃-B₂O₃:V₂O₅ glasses.

Glass	g	g _⊥	Δg /Δg _⊥
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_{||}/g_⊥ ratio is observed to decrease gradually with increase in the concentration of V₂O₅ which is an indication of increase in tetragonal distortion around vanadyl ions. The increase in the intensity of the signal with the concentration of V₂O₅ 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 BO₃ structural units at the expense of BO₄ units, in fact supports this view point.

4 Conclusions

The density of present glasses is increasing with increase in the mol% of V₂O₅ almost linearly. The molar volume of the glass samples is decreasing where as the oxygen packing density is increasing with increase in the vanadium ion concentration.

The increase in electronic polarizability with increase in the mol% of V₂O₅ indicates that the electron cloud is more easily deforming with concentration of V₂O₅. The B₂O₃ is a strong acidic oxide with low optical basicity (0.43) whereas V₂O₅ is an oxide with significant optical basicity (1.04). The increase in the optical basicity of the glasses with increase in V₂O₅ concentration indicates the acid- base properties of V₂O₅ 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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