

Spectroscopic and Bonding Properties as A Probe in the Symmetry of PbO-P₂O₅-ZnO- V₂O₅ Glass System With Alkali Oxides

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ABSTRACT: PbO-P₂O₅-ZnO-V₂O₅ glasses composed of different alkali oxides are prepared. The glasses are characterized by XRD, FTIR, EPR and UV-Visible spectral analysis. The functions of structural features and amorphous nature due to compositional changes are examined using XRD. FTIR spectroscopy is used to identify the presence of bond assignments and vibrational modes of phosphate in the system. Depolymerization of the phosphate network by the replacement of alkali oxide content in the glasses which are consisting mainly more of (PO₄³⁻) and (PO₃²⁻) units, is detected by the FTIR spectra. The spectral studies have exhibited an intense and broadband in the visible region which is related to VO²⁺ ions in a ligand field of C_{4v} symmetry. The importance of bridging oxygen in improving the optical properties is studied.

KEYWORDS: Phosphate Glass; FTIR; UV-Vis and EPR spectra; Bonding properties.

I. INTRODUCTION

Vibrational spectroscopic studies (FTIR) for vitreous P₂O₅, are useful to distinguish bridging and terminal oxygen atoms [1-2]. Electron paramagnetic resonance (EPR) is already proved to provide answers to significant questions about structure by showing the influence of electron spin-spin interactions between paramagnets. Thus, an investigation on the relationship between the composition and properties of these materials is seen to be important. Phosphate glasses have attracted considerable attention in recent years due to their nonlinear optical properties. Oxide glasses with large non-linear refractive index and non-linear absorption coefficient are used for optical fibre telecommunication and for non-linear optical devices such as ultra fast optical switches, power limiters, real time holography, self-focusing, white-light continuum generation and photonic applications [3-5]. As an extension of work [6,7], the present paper is to study the properties of VO (II) as dopant in Pb₃O₄-M₂O-ZnO-P₂O₅ (where M=Li, Na and K) glasses (hereafter referred to as LPZ, NPZ and KPZ glasses) through various spectroscopic techniques like Electron Paramagnetic Resonance and Optical absorption and also to identify the importance of Pb (II-IV) in heavy metal combinations. This sort of information is useful to determine the microscopic insight of glasses for different nonlinear optical applications as well as for optical fibre amplifiers.

II. EXPERIMENTAL

The chosen materials are -Pb₃O₄, ZnO, V₂O₅, Na₂CO₃, Li₂CO₃, K₂CO₃ and P₂O₅ of 99.9% Analar grade in this study. The host glass composition is taken as 10 Pb₃O₄ + 20 M₂O + 10 ZnO + 59.9 P₂O₅ + 0.1 V₂O₅ (where M = Li, Na and K). For each concentration the mixture is firstly sintered at 700 K after being thoroughly mixed by quench melting method. Then the sample is taken into a porcelain crucible and melted in an electric furnace at 1200 K for nearly 1hour. For quenching, the melt glass is formed at room temperature in air. Thereafter, the glass material is annealed at 550 K for 30 minutes. To ascertain amorphous nature of the glass, X-ray diffraction studies are performed through PHILIPS

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X'PERT PRO X-RAY diffraction system. The Fourier Transform Infrared spectra of these glasses are recorded on SHIMADZU 8201 PC FTIR Spectrophotometer in the range 4000-400 cm^{-1} using KBr pellets. EPR spectra are recorded at room temperature through JES-FA series X-band EPR spectrometer having 100 kHz field modulation. Optical absorption spectra of these glasses are recorded at room temperature through JASCO (V-530) spectrophotometer in UV-Visible region.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of VO^{2+} doped alkali lead zinc phosphate glass system. As no significant crystalline peaks are recorded in the patterns, the amorphous nature of glass samples is confirmed here.

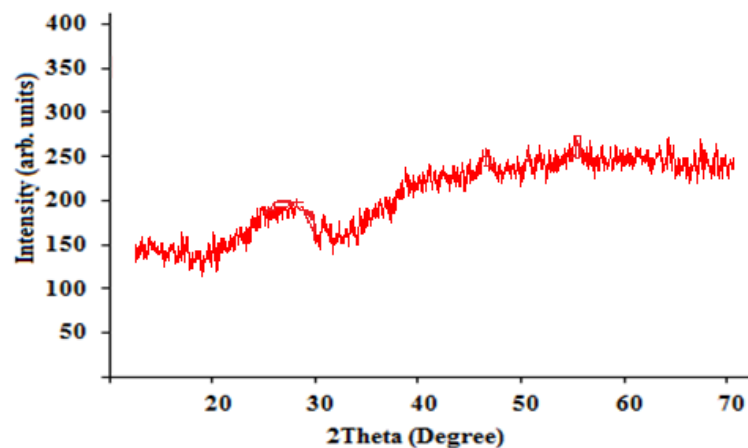


Fig. 1 XRD spectrum of VO (II) ion in Alkali Lead Zinc Phosphate Glasses

The tendency of strong depolymerisation of the glass network by introducing alkali (Li, Na and K) oxides is also confirmed by the FTIR spectra (Fig. 2). The bands and their assignments are 1230 cm^{-1} caused due to (P-O) vibrations; 1060 cm^{-1} bands to PO_4^{3-} fundamental vibrational mode; 880 cm^{-1} to asymmetric stretching vibrations of P-O-P groups; 770 cm^{-1} a symmetric vibration to P-O-P chains and 600 cm^{-1} to bending vibration of the P-O-P bonds [8-10]. FTIR study has, hence, established that alkali oxide entered into the network interstitially as a network modifier and later, depolymerisation is initiated by breaking of P-O-P linkages.

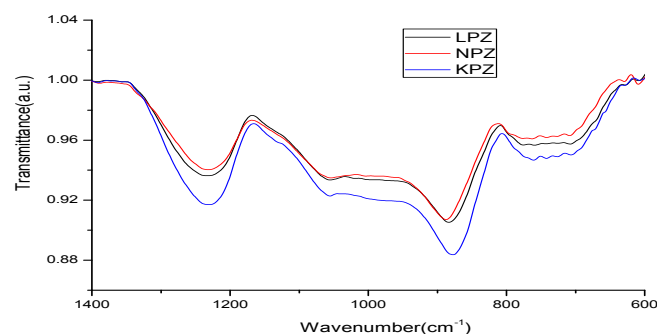


Fig. 2 FTIR spectra of VO (II) ion in Alkali Lead Zinc Phosphate Glasses

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Vanadium in tetravalent state exists almost exclusively as the vanadyl ion VO^{2+} which is formed when the V^{4+} with a single unpaired $3d$ electron is bound to oxygen by strong covalent bond. According to Selbin [11], this species is the most stable diatomic radical. Vanadium ions act as network modifiers but also as network formers depending on their concentration in the glass matrix. The ESR spectrum of V^{4+} in glasses has shown rich hyperfine structure due to the ^{51}V nucleus ($I = 7/2$) which is easily observable in most systems at room temperature. The EPR spectra obtained at room temperature for alkali lead zinc phosphate glasses with a small content of V_2O_5 has shown a well resolved hyperfine structure typical for isolated vanadium ion in a ligand field of C_{4v} symmetry, presented as vanadyl ion as shown in Figure 3. The spin-Hamiltonian is described in a way like

$$H = \beta [g_{\parallel} B_z S_z + g_{\perp} (B_x S_x + B_y S_y)] + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y) \quad (1)$$

here β is the Bohr magneton while g_{\parallel} , g_{\perp} and A_{\parallel} , A_{\perp} are the components of the gyromagnetic tensor g and hyperfine structure tensor A , respectively. B_x , B_y and B_z are components of the magnetic field; S_x , S_y , S_z and I_x , I_y , I_z are the spin operators of the electron and the nucleus, respectively.

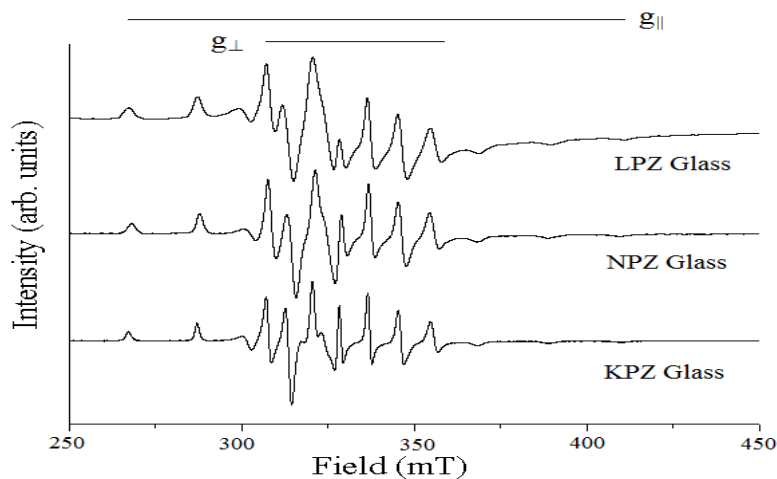


Fig. 3 EPR spectra of VO (II) ion in Alkali Lead Zinc Phosphate Glasses

The spin-Hamiltonian and hyperfine values are evaluated from EPR spectra of vanadyl doped Alkali Lead Zinc Phosphate glass and shown in Table 1. An octahedral site with a tetragonal compression would give the values of $g_{\parallel} < g_{\perp} < g_e$. The present values of the spin-Hamiltonian parameters have agreed with the relation. Furthermore, the values of A_{\perp} interaction matrices have the relation $A_{\parallel} > A_{\perp}$ for all those three samples. These observations have led to the conclusion that the paramagnetic V^{4+} ion in the glass has been present as vanadyl ion $[VO(II)]$, in an octahedral environment of oxygens with tetragonal distortion where the vanadyl oxygen forms the apex V-O bond [12-14]. The dipolar coupling constant (P) and Fermi-constant coupling parameter (κ) are evaluated using the following formulae [15].

$$A_{\parallel} = P [(-4/7) - \kappa + (g_{\parallel} - g_e) + (3/7) (g_{\perp} - g_e)] \quad (2)$$

$$A_{\perp} = P [(2/7) - \kappa + (11/14) (g_{\perp} - g_e)] \quad (3)$$

where $g_e = 2.0023$

Table1: spin-Hamiltonian and hyperfine values of VO (II) ion in Alkali Lead Zinc Phosphate Glasses

Glass Sample	g_{\parallel}	g_{\perp}	A_{\parallel} $\times 10^{-4} \text{ cm}^{-1}$	A_{\perp} $\times 10^{-4} \text{ cm}^{-1}$	κ	P
LPZ Glass	1.9298	1.9761	185	63	0.73	-133.7
NPZ Glass	1.9302	1.9753	182	61	0.73	-131.6
KPZ Glass	1.9301	1.9757	184	62	0.73	-132.5

The lower values of κ have indicated the poor contribution of vanadium 4s orbital to the vanadyl bond in these glasses. It has also suggested that a hexa-coordinated geometry for the VO (II) ion in the complex of near octahedral (O_h) symmetry which is due to the weakness of the V-O bond in the vanadyl group caused by a strong axial perturbation arising from the sixth oxygen atom has coordinated in the transposition to the vanadyl oxygen [6,16]. The single d-electron of the VO^{2+} ion occupies the t_{2g} orbital in the octahedral crystal field giving rise to ${}^2T_{2g}$ ground state. When excited, the electron occupies the upper e_g orbital giving rise to 2E_g term. In ideal octahedral symmetry, only one band is expected to arise from the transition ${}^2T_{2g} \rightarrow {}^2E_g$. However, VO^{2+} never exhibits an ideal octahedral symmetry but lowers to tetragonal (C_{4v}) or still lower symmetries like C_{2v} because of the non-symmetrical alignment of the V=O bond. In C_{4v} symmetry, ${}^2T_{2g}$ splits into 2B_2 and 2E , where as 2E_g splitting into 2B_1 and 2A_1 . Accordingly three bands are expected due to the transitions from the ground state (2B_2) to the excited states 2E , 2B_1 , and 2A_1). The general ordering of energy levels is as follows [15, 17]: ${}^2B_2 < {}^2E < {}^2B_1 < {}^2A_1$. Optical absorption spectra are shown in Figure 4. Here the recorded spectrum has revealed only two bands which are characteristic of VO (II) ion in tetragonally distorted octahedral site. The bands are attributed to the transitions ${}^2B_2 \rightarrow {}^2E$ and ${}^2B_2 \rightarrow {}^2B_1$ respectively.

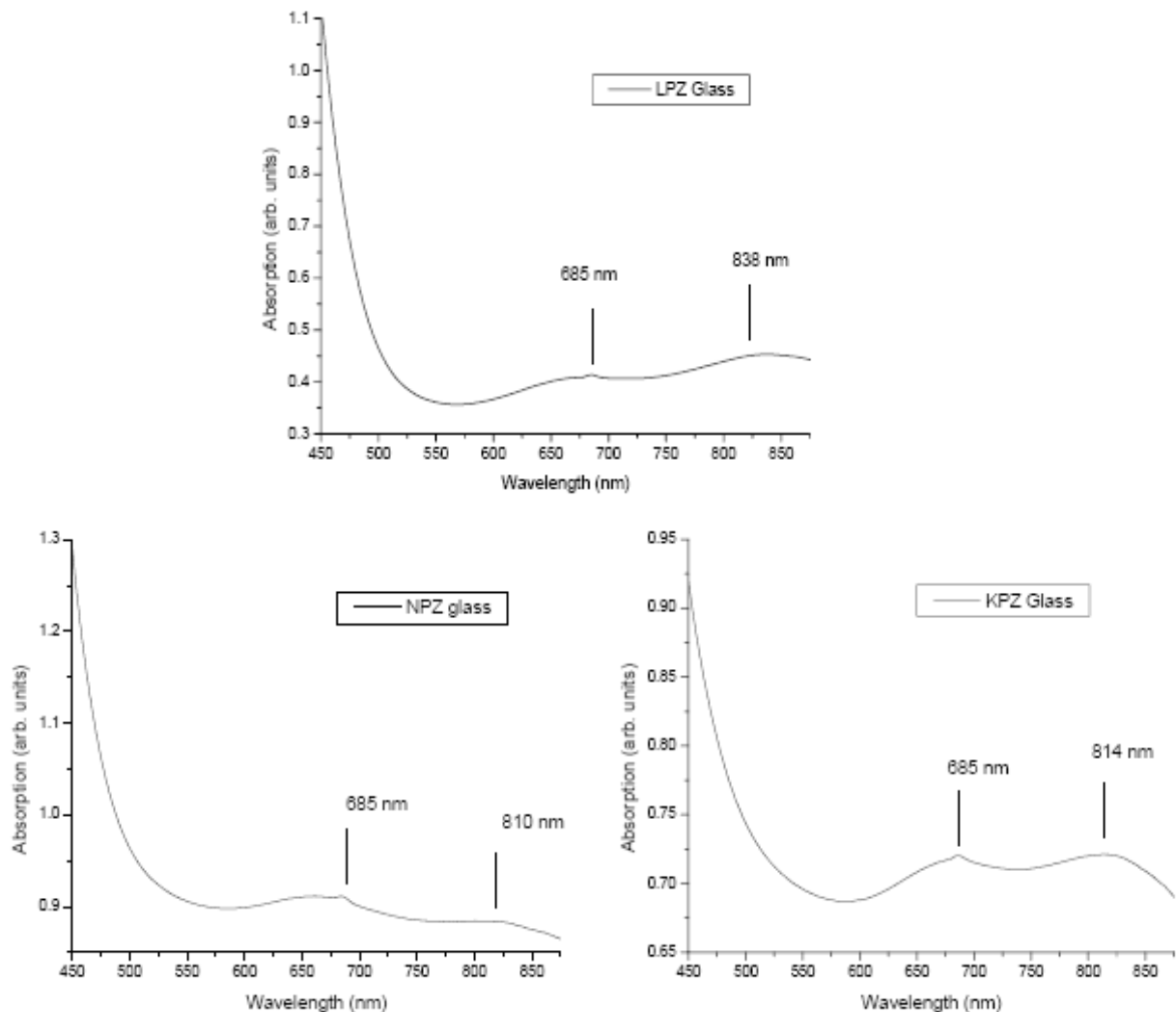


Fig. 4. Optical absorption spectra of VO (II) ion in Alkali Lead Zinc Phosphate Glasses

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The values of EPR parameters and the covalency degrees of the in- plane V-O σ -bonds (β^{*2}) and of π -bonding (ϵ_{π}^{*2}) with the equatorial ligands are equal to unity when the bonding is purely ionic. For a completely ionic π bond between the vanadium and vanadyl oxygen (ϵ_{π}^{*2}) would be equal to unity. These coefficients represent value of 0.5 for a completely covalent bond. These parameters are evaluated with the help of Molecular Orbital scheme developed by Kivelson and Lee [16].

$$\beta^{*2} = \frac{\left(1 - \frac{g_{\parallel}}{g_e}\right)\Delta_{\parallel}}{4\lambda} ; (4) \quad \epsilon_{\pi}^{*2} = \frac{\left(1 - \frac{g_{\perp}}{g_e}\right)\Delta_{\perp}}{\lambda} ; (5)$$

here the free ion value of spin orbit coupling constant for VO(II) ion is $\lambda = 170 \text{ cm}^{-1}$. Δ_{\parallel} and Δ_{\perp} for the energies of the electronic transitions ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2E$ respectively. The evaluated values are noted down in Table 2.

Table 2: Bonding parameters for VO(II) ion in Alkali Lead Zinc Phosphate Glasses

Glass Sample	β^{*2}	ϵ_{π}^{*2}
LPZ Glass	0.77	0.91
NPZ Glass	0.77	0.97
KPZ Glass	0.77	0.96

Electron paramagnetic resonance and optical absorption studies have indicated covalent nature from both g-values and bonding parameter values. LPZ glasses have more covalent nature when compared to others due to the presence of Pb^{4+} which developed the bridging oxygens. Therefore two states of Pb_3O_4 as Pb^{2+} and Pb^{4+} ($2\text{PbO} + \text{PbO}_2$) are the major assets to have increased the lead concentration. When PbO entered the network, it is noticed to form PbO_4 units in which lead is coordinated to four oxygens in a covalently bonded configuration. It is understood that lead did not reside in the glass network interstitially. For a constant content of P_2O_5 , the substitution of ZnO by PbO has led to an increase in the network disorder. The changes in network structure, bonding nature, high amorphous character and increasing optical behaviour might have occurred due to not only by the presence of Pb^{4+} but also by alkali content which is deemed to be helpful in depolymerisation of phosphate network. Lithium is more effective than sodium and potassium in breaking the phosphate network because of its low ionic radius ($\text{Li} < \text{Na} < \text{K}$) and acting as modifier. Hence, it is unambiguous that the bridging oxygens caused by Pb^{4+} have developed $\text{Pb}^{2+} - \text{O} - \text{Pb}^{4+} - \text{O} - \text{Pb}^{2+}$ and $\text{Pb} - \text{O} - \text{Zn}$ chains linking the phosphate tetrahedral in a covalent bond configuration. The present spectroscopic studies have also revealed the same nature and indicating the decrease in network connectivity for this alkali lead zinc phosphate glass system. As lead partially participated in the network formation [18] and decomposed into nano scale separated entities, these entities have accounted for higher optical properties [18,19] for LPZ glass sample. Lead phosphate glasses possess enhanced optical non-linearity due to high polarizability of Pb^{2+} ions in glass matrices. Electrostatic interaction between transition metal ion and the highly excited Pb^{4+} ions is also known to cause this result [20].

The data of physical properties presented in Table 3 have indicated that the average molecular weight increases from LPZ to KPZ glass which influences density and other physical parameters. The increase in density for the glass system has shown the change in the structure of the glass with replacement of alkali content. It is evident that the mean atomic volume and optical basicity of the glasses increased with the replacement of alkali oxide. The theoretical value of optical basicity (Λ_{th}) reflects the ability of the glass to donate negative charge to the probe ion. The basicity parameter from Duffy and Ingram increased from glass to glass [21]. High optical basicity means high electron donor ability of the oxide ions to the cations [22]. Variations in physical properties are due to replacement of alkali oxides in different glasses around VO (II) ions

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Table 3. Physical properties of VO (II) ion in Alkali Lead Zinc Phosphate Glasses

Physical Property	LPZ Glass	NPZ Glass	KPZ Glass
Refractive Index (N) At 589.3 nm	1.6231	1.6196	1.5961
Density (D) (gm/cm ³)	3.2356	3.2870	3.3030
Average Molecular Weight (M gm)	167.8821	174.3017	180.7451
Ion Concentration (N)x10 ²¹ ions/cm ³	1.1608	2.2716	3.3020
Mean Atomic Volume (gm/cm ³ /atom)	9.1026	9.3029	9.6001
Optical Dielectric Constant	1.6344	1.6231	1.5475
Dielectric Constant (ε)	2.6344	2.6231	2.5475
Reflection Loss (R %)	5.6426	5.5943	5.2722
Molar Reflection (Rm cm ⁻³)	18.2985	18.6169	18.6215
Polaron Radius (Rp Å)	3.8345	3.0656	2.7063
Interionic Distance x10 ⁻⁸ (R _i Å)	9.5150	7.6070	6.7154
Molecular Electronic Polarizability (x10 ²³ cm ³)	7.2529	3.6895	2.4603
Field Strength (x10 ¹⁵ cm ⁻²)	1.3602	2.1280	2.7307
Optical Basicity	0.5197	0.5211	0.5251

IV. CONCLUSIONS

FTIR spectra have showed that the replacement of alkali oxides has depolymerised the phosphate glass network, due to breaking of P-O-P bonds and development of more new bonds. EPR studies have shown that $g_{\perp} > g_{\parallel}$ are representing tetragonally compressed octahedral site for the VO²⁺ ion. Thus, the inference is that vanadium enters the glasses as VO (II) ion. The value of ($g_{\perp} - g_{\parallel}$) indicates the tetragonal distortion existence in the present glass matrix. The optical absorption spectra also suggest the same with characteristic band transitions from ²B₂ and the site symmetry for C_{4v}. Only two transitions are observed. The FTIR results have supported similarly as both the results obtained from the EPR and optical absorption which inferred the major role of alkali in the formation of cross linking bands. The covalence degree of the in-plane V-O σ-bonds (β^{*2}) and π-bonding with the vanadyl oxygen ($\epsilon_{\pi^{*2}}$) in the glass has indicated the covalent nature. The presence of heavy metal oxide combinations causes the occupation of most of the volume of the network to improve the optical nature of the glass and durability. Lastly, therefore, LPZ glass is more suitable glass matrix for enhanced nonlinear optical applications like dispersion.

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