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Spectroscopic investigations of the $PbO–MoO_3–P_2O_5:V_2O_5$ glass system

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V_2O_5 doped $PbO–MoO_3–P_2O_5$ glasses were prepared by melt-quenching and the amorphous nature of these samples was confirmed by XRD. EPR data indicate the presence of V^{4+} ions in a square-pyramidal coordination (C_{4v}). The experimental EPR spectra were simulated assuming a superposition of two signals; one with hyperfine structure (HFS) typical for isolated ions and the other one consist of a broad line without HFS characteristic of clustered ions. The optical absorption spectra of the glasses exhibited two broad absorption bands corresponding to $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2E$ transitions of VO^{2+} ions, with increasing concentration of V_2O_5, the half width and peak height of these bands were observed to increase. The IR bands of phosphate groups were strongly reduced for 0·6 mol% of V_2O_5 due to the depolymerisation of the phosphate network and to the appearance of new vibrations characteristic of P–O–V and V–O–V linkages showing the network former role of V_2O_5.

1. Introduction

Phosphate glasses have superior physical properties such as low melting temperature, high thermal expansion coefficient, strong glass forming ability, high electrical conductivity and simple structure. Because of this, phosphate glasses have attracted increased recent attention compared with silicate or borate glasses[1–4] and also these properties make them useful candidates for fast ion conducting materials.[5] During the last two decades phosphate glasses have been investigated intensively, but there is still a great interest in developing new glasses related to the demands of both industry and technology. These glasses have poor chemical durability that often limits their usefulness, but which can be improved by the substitution of various oxides such as lead oxide.[6,7] In the last decades lead oxide was not only used as a constituent in several borate glasses,[8,9] but also in phosphate glasses[10] in order to reach new and useful physical and chemical properties for technological applications. The structural role of PbO in many oxide glasses is interesting because it has been demonstrated that it plays a dual role, as network modifier and the former.[11] Several interesting properties of phosphate glasses have been found to result from the incorporation of PbO into the glass network. For instance, PbO is useful for shielding against high energy radiations, including nuclear radiation[12] and its addition may result in the formation of P–O–Pb bonds. These bonds also lead to an improvement of the chemical durability of phosphate glasses.[13]

The introduction of MoO_3 in phosphate glasses leads to the formation of various molybdenum units that enter into the glass network by crosslinking phosphate chains.[14,15] Infrared spectroscopic investigations of a few PbO modified molybdophosphate glasses reveals that the addition of the modifier depolymerises the phosphorous–oxygen chain by forming new P–O–Pb bonds and nonbridging oxygens in the network.[16] A few studies of the compositional dependence of the glass network structure in a few molybdophosphate glasses show that increasing MoO_3 content leads to the transformation of Mo–O– and P–O bonds into Mo–O–Mo and weaker Mo–O–P bridging bonds.[17,18] Semiconducting transition metal oxide glasses have gained importance in recent years due to their possible applications in various technological fields.[19–22] Transition metal ions are very interesting ions to probe in glass networks because of their broad radial distribution of outer d-orbital electron functions and their sensitive response to the surrounding cations.[23–26] Among various semiconducting transition metal oxide glasses, vanadate glasses find applications in memory and switching devices. V_2O_5 is known to participate in the glass network with VO_5 pyramidal structural units. Several vanadate glasses show semiconducting behaviour with electrical conductivities of 10^{-3}–10^{-5} $(W\,cm)^{-1}$, which is known to be due to electron hopping between V^{4+} to V^{5+} ions in the glass network. The content of vanadium in different valence states in the

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glass depends upon the quantitative properties of the modifiers and glass formers in the glass, the size and field strength of the ions in the glass structure, mobility of the modifier cation, etc. Hence, the connection between the state and the position of the vanadium ion and the structure and physical properties of the glass is expected to be highly interesting. Moreover, vanadium glasses are identified as n-type semiconductors for low values of the V^{4+}/V^{5+} ratio. Vanadium ions may also be present in the glass network in V^{2+} and V^{3+} states.[27]

The objective of the present study is intended to investigate quantitatively the spectroscopic properties, viz. optical absorption, electron spin resonance (ESR) spectra and infrared spectra of $PbO–MoO_3–P_2O_5$ glasses containing different concentrations of V_2O_5. The infrared spectral techniques can be used for obtaining information on the structural details of these glasses as they are very sensitive to the local symmetry, the character of the chemical bond and other structural properties. Information about the valence state and the distribution of the vanadium ion depending on their concentration can be obtained by means of optical absorption and ESR measurements.

2. Experimental methods

The glass samples of compositions used for the present study are $30PbO–5MoO_3–(65–x)P_2O_5:xV_2O_5$ where x ranges from 0–1·0 mol%; the samples are labelled as V_0 (x=0), V_2 (x=0·2), V_4 (x=0·4), V_6 (x=0·6), V_8 (x=0·8) and V_{10} (x=1·0). The glasses used in the present measurements are prepared by melting and quenching. Reagent grade PbO, MoO_3, P_2O_5 and V_2O_5 were thoroughly mixed in appropriate proportions and melted in a thick walled platinum crucible in the temperature range 950–1000°C in a PID temperature controlled furnace for about 30 min until a bubble free liquid was formed. The resultant melt was then poured into a brass mould and subsequently annealed at 300°C with a cooling rate of 1°C/min. 1×1×0·2 cm samples prepared were ground and optically polished. The amorphous nature of samples was verified by x-ray diffraction (XRD) using a Rigaku D/Max ULTIMA III x-ray diffractometer with Cu K_α radiation.

Differential thermal analysis (DTA) was carried out using STA 409C model DTA-TG instrument with a programmed heating rate of 10°C/min, in the temperature range 30–1000°C to determine the glass transition temperature and other glass forming ability parameters. The optical absorption spectra of the samples were recorded at room temperature in the wavelength range 300–2200 nm to a resolution of 0·1 nm using a JASCO Model V-670 UV-vis-NIR spectrophotometer. The ESR spectra of fine powders of the samples were recorded at room temperature on E11Z Varian X–band (ν=9·5 GHz) ESR spectrometer. Infrared transmission spectra were recorded on a Bruker IFS 66 V–IR spectrophotometer with a resolution of 0·1 cm^{-1} in the range 400–2000 cm^{-1} using potassium bromide pellets (300 mg) containing pulverized glass (1·5 mg). The details of methods adopted for recording DTA, IR, ESR and optical absorption measurements were similar to those reported in our earlier papers.[28]

Table 1. Summary of physical parameters data for $PbO–MoO_3–P_2O_5:V_2O_5$ glasses

Glass	Density (g/cm^3)	Avg. Mol. Weight	N_i ($10^{21}/cm^3$)	R_i (Å)
V_0	4·572	163·12	--	--
V_2	4·579	162·99	3·38	6·66
V_4	4·587	162·87	6·78	5·28
V_6	4·595	162·74	10·2	4·61
V_8	4·603	162·62	13·6	4·19
V_{10}	4·611	162·49	17·1	3·88

3. Results

From the measured values of density d and calculated average molecular weight of the glasses various physical parameters such as vanadium ion concentration N_i and mean vanadium ion separation R_i in these glasses are evaluated using the conventional formulae[29] and are presented in Table 1.

The thermal analysis results of all the glasses under study are shown in Figure 1. The curves show an endothermic effect due to the glass transition temperature T_g in all samples. Further at higher temperatures an exothermic peak T_c is for the crystal growth and an endotherm, due to melting T_m were also detected. All the glasses exhibit the glass transition temperature T_g between 335 and 355 K. From the measured values of T_g, T_c and T_m, and the parameters ($T_c–T_g$), ($T_m–T_c$) and Hruby's parameter (Hruby, 1972; the glass forming parameter) $K_{gl}=(T_c–T_g)/(T_m–T_c)$, which give information on the stability of the glass against divitrification[30] were evaluated and are presented in Table 2. The good homogeneity of all the glass samples prepared is proved by the appearance of single peak due to the glass transition temperature in the DTA traces of all the glasses. Generally, unstable glasses show a crystallisation peak close

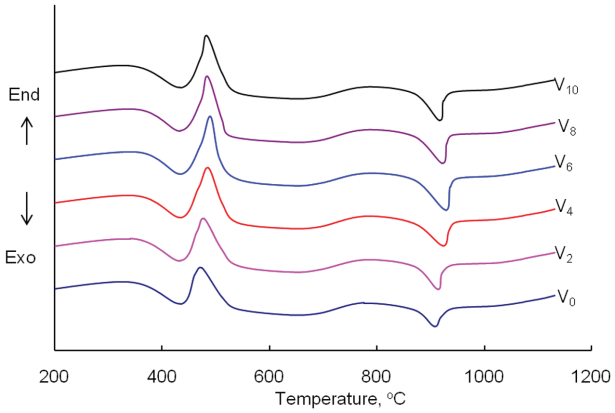

Figure 1. DTA patterns of $PbO–MoO_3$-P_2O_5 glasses containing different concentrations of V_2O_5 [Colour available online]

Table 2. Summary of differential thermal analysis data for $PbO–MoO_3–P_2O_5:V_2O_5$ glasses

Glass	T_g /K	T_c /K	T_m /K	$K_{gl}=(T_c–T_g)/(T_m–T_c)$
V_0	338	473	907	0·3111
V_2	341	478	914	0·3142
V_4	348	486	923	0·3158
V_6	351	490	928	0·3173
V_8	349	485	922	0·3112
V_{10}	348	483	918	0·3103

to the glass transition temperature. Therefore, the temperature difference $T_c–T_g$ is a good indication of thermal stability because the higher the value of this difference, the greater the delay in nucleation (Mehta *et al*, 2006). This parameter shows that thermal stability of the sample The variation in the parameter K_{gl} with the variation of concentration of V^{4+} ion shows the maximum value for glass V_6, as it increases with increasing vanadium concentration from 0·1 to 0·6 mol% and beyond 0·6 mol% V_2O_5 it decreases.

Figure 2 represents the optical absorption spectra of $PbO–MoO_3–P_2O_5:V_2O_5$ glass samples recorded at room temperature in the wavelength region 300–1200 nm. The absorption edge of the glass V_0 noticed at 406 nm had shifted to 375 nm by glass V_6; further increases in the concentration of V_2O_5 makes the edge shift gradually towards longer wavelengths. The spectra of all the glasses had absorption bands between 600 and 625 nm and a band between 970 and 1000 nm due to V^{5+} ion transition. The spectrum of glass V_6 exhibited two broad absorption bands with the meta-centres at 598 and 972 nm (Table 3) corresponding to $^2B_2\rightarrow{}^2B_1$ and $^2B_2\rightarrow{}^2E$ transitions of VO^{2+} ions.[31] From the observed absorption edges, we have evaluated the optical band gaps (E_o) of these glasses by drawing Urbach plot between $(a\hbar w)^{1/2}$ and $\hbar w$ as per the equation:

$$\alpha(\omega)\hbar\omega=C(\hbar\omega–E_o)^2 \quad (1)$$

From the extrapolation of the linear portion of the curves of Figure 3, the values of optical band gap (E_o) were determined and are presented in Table 3. As the

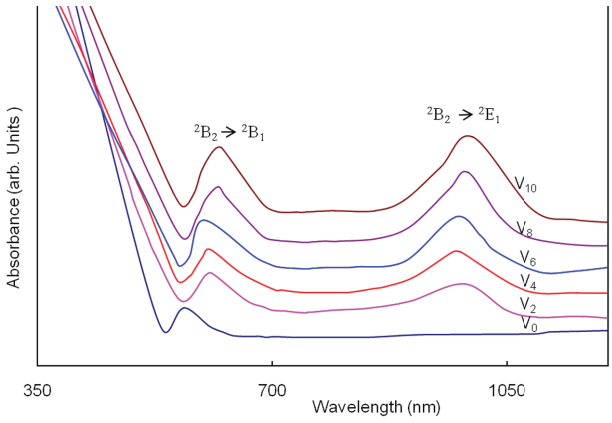

Figure 2. Optical absorption spectra of $PbO–MoO_3–P_2O_5$ glasses containing different concentrations of V_2O_5 [Colour available online]

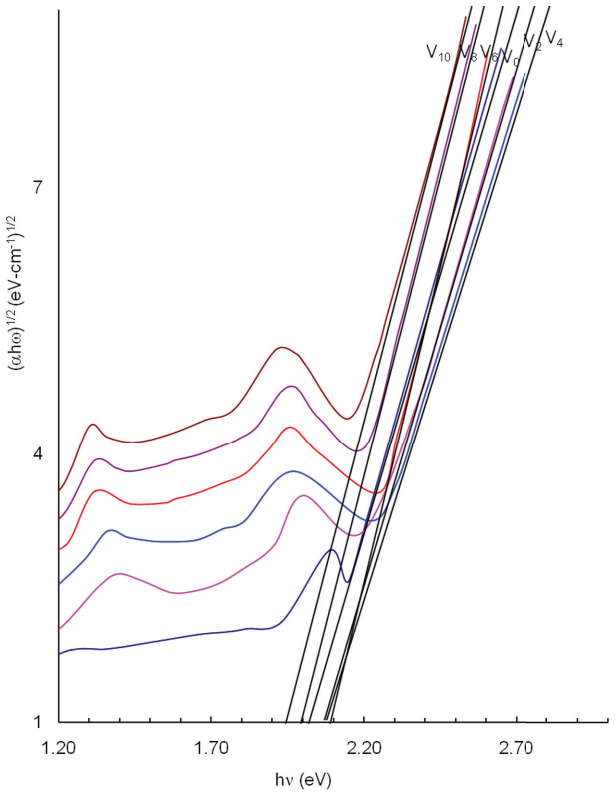

Figure 3. Plots to evaluate optical band gaps of $PbO–MoO_3–P_2O_5$ glasses containing different concentrations of V_2O_5 [Colour available online]

concentration of vanadium oxide increases the value of E_o is found to increase up to 0·6 mol% beyond that it decreases.

The infrared transmission spectra of $PbO–MoO_3–P_2O_5:V_2O_5$ glasses (Figure 4) exhibit vibrational bands around 1310 cm^{-1} (band due to antisymmetrical vibrations of PO_2^- groups, this region may also consist of bands due to P=O stretching vibrations), 1040 cm^{-1} (a normal vibrational mode of symmetrical stretching vibrations of PO_2^- in PO_4^{3-} groups), at 943 cm^{-1} due to P–O–P asymmetric vibrations.[32–35] Incidentally the band due to P–O–P symmetric stretching vibrations also lies around 700 cm^{-1}.[36] Due to the intermediate nature of glass former MoO_3, two new bands have also been located at 810 and 881 cm^{-1} in the spectrum of glass V_6; these bands have been attributed to n_1 and n_3 vibrational modes of MoO_4^{2-} tetrahedral units respectively.[37–39] In the present glass system the percentage of the molybdenum is very small hence these two bands not influence the glass system. With

Table 3. Summary of optical absorption spectra data for $PbO–MoO_3–P_2O_5:V_2O_5$ glasses

Glass	Cut-off wavelength (nm)	Optical band gap E_o (eV)	Position of $^2B_2\rightarrow{}^2B_1$ band (nm)	Position of $^2B_2\rightarrow{}^2E$ Band (nm)
V_0	406	2·02	-	-
V_2	394	2·05	612	986
V_4	382	2·07	607	979
V_6	375	2·10	598	972
V_8	414	1·98	619	991
V_{10}	426	1·95	625	997

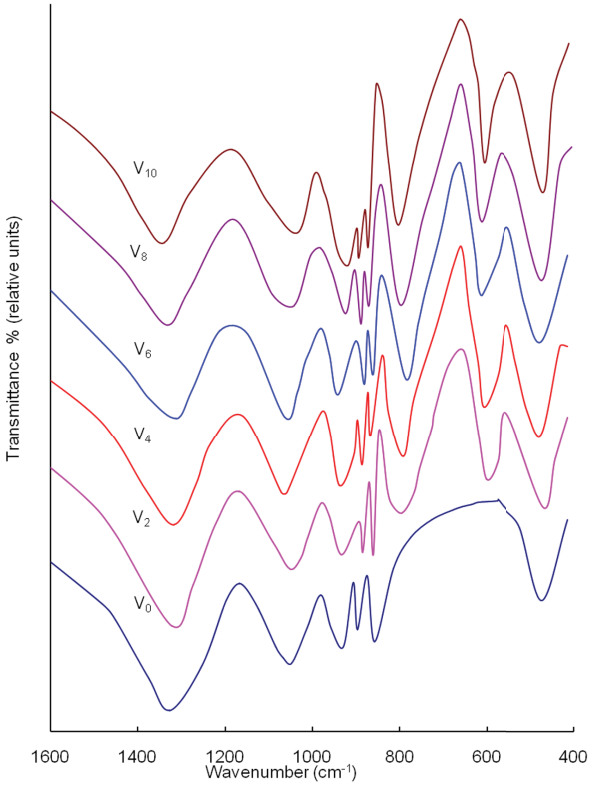

Figure 4. Infrared spectra of PbO–MoO_3-P_2O_5 glasses containing different concentrations of V_2O_5 [Colour available online]

the gradual increase of V_2O_5 in the PbO–MoO_3–P_2O_5 glasses, the following changes were observed in the spectra: (i) a considerable decrease in the intensity of the band due to P=O stretching vibrations, (ii) the band due to P–O–P asymmetric vibrations shifted towards lower wavenumbers with increasing intensity, (iii) up to nearly 0·6 mol% of V_2O_5 no notable change in the intensity PO_4^{3-} band was observed; however, beyond this concentration the intensity of this band clearly decreased. Further an intense absorption band with a meta-centre at about 780 cm^{-1} related to V–O–V chains and a weak band at about 600 cm^{-1} corresponding to bending vibrations of the vanadium ions[40] have also been observed. In the region of symmetric stretching vibrations of PO_4^{3-} units (at about 1040 cm^{-1}) a band due to vibrations of isolated V=O groups in the VO_5 trigonal bipyramids is also expected.[41] A kink at about 472 cm^{-1} is formed due to PbO_4 units. A summary of the data on the positions of various bands in the infrared spectra of PbO–MoO_3–P_2O_5 glasses doped with different concentrations of V_2O_5 is presented in Table 4.

The ESR spectra (recorded at room temperature) for PbO–MoO_3–P_2O_5 doped with different concentrations of vanadium oxide glasses under investigation are shown in Figure 5; the spectra are observed to be complex made up of resolved hyperfine components arising from the unpaired $3d^1$ electron of the ^{51}V isotope whose spin is 7/2. As the concentration of V_2O_5 is increased, an increasing degree of resolution and

Table 4. Summary of infrared spectra absorption band positions in cm^{-1} for PbO–MoO_3–P_2O_5:V_2O_5 glasses

Assignment	*Glass V_0*	*Glass V_2*	*Glass V_4*	*Glass V_6*	*Glass V_8*	*Glass V_{10}*
PO_2^-/P=O stretching	1326	1321	1317	1312	1330	1338
PO_4^{3-} groups	1046	1052	1058	1062	1041	1035
P–O–P asymmetric bending	928	933	938	942	922	917
MoO_4 ($\upsilon 1$)	897	892	886	881	903	909
MoO_4 ($\upsilon 3$)	820	816	813	810	826	831
V–O–V chains	-	793	789	785	798	804
V–O–V bending	-	611	607	600	616	619
PbO_4 units	472	472	472	472	472	472

signal intensity were observed. The values of $g_{\parallel}$ and $g_{\perp}$ (obtained from these spectra) along with the other pertinent data are given in Table 5.

4. Discussion

P_2O_5 is a well known network former with PO_4 structural units with one of the four oxygen atoms in PO_4 tetrahedron being doubly bonded to the phosphorus atom with substantial p-bond character to account for the pentavalency of phosphorous.[42] The PO_4 tetrahedra are linked together with covalent bonding in chains or rings by bridging oxygens. Neighbouring phosphate chains are linked together by cross bonding between the metal cation and two nonbridging oxygen atoms of each PO_4 tetrahedron.

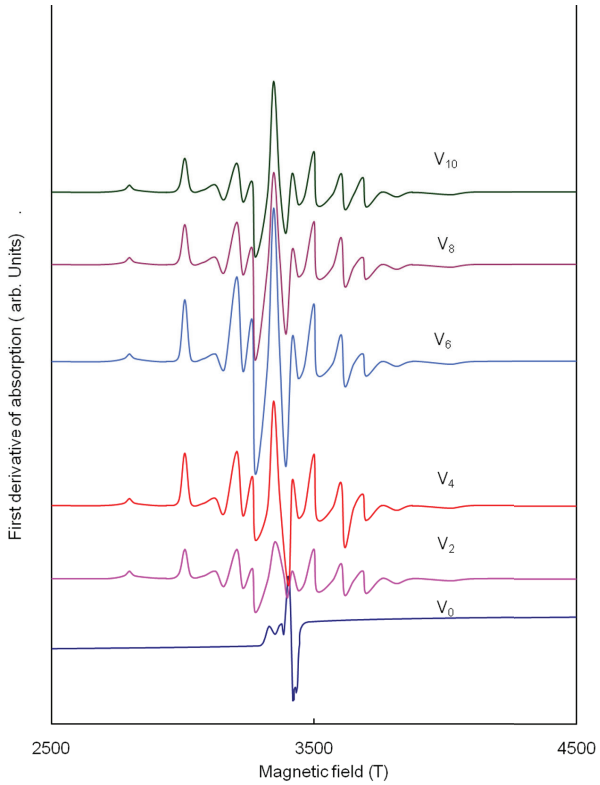

Figure 5. ESR spectra of PbO–MoO_3–P_2O_5:V_2O_5 glasses [Colour available online]

Table 5. ESR spectra data of $PbO–MoO_3–P_2O_5:V_2O_5$ glasses

Glass	$g_{\|\|}$	$g_\perp$	$\Delta g_{\|\|}$	$\Delta g_\perp$	$\Delta g_{\|\|}/\Delta g_\perp$
V_2	1·914	1·995	0·024	0·017	1·41
V_4	1·912	1·993	0·027	0·019	1·42
V_6	1·911	1·992	0·032	0·021	1·52
V_8	1·917	1·996	0·020	0·015	1·33
V_{10}	1·920	1·998	0·015	0·013	1·15

In general the P–O–P bond between PO_4 tetrahedra is much stronger than the cross bond between chains via the metal cations.[43]

PbO in general is a glass modifier and occupies octahedral positions in the glass network. As a modifier it enters the glass network by transforming two Q^3 tetrahedra (viz. PO_4 tetrahedra with three bridging oxygens and one terminal bonded oxygen) into two Q^2 tetrahedra (viz. PO_4 tetrahedra with two bridging oxygens and two terminal bonded oxygens) and thus a PbO polyhedron is formed when is it surrounded by two Q^2 and several Q^3 tetrahedra. This structure behaves like a defect in the P_2O_5 network. To form octahedral units, Pb should be sp^3d_2 hybridized (6s, 6p and 6d orbitals).[44,45] However, PbO may also participate in the glass network with PbO_4 structural units when the lead ion is linked to four oxygens in a covalent bond configuration.

Vanadium ions are expected to be present mainly as V^{5+} in the present $PbO–MoO_3–P_2O_5$ glass network. However, during the melting of the glasses at higher temperatures there is every possibility of the following redox equilibrium taking place:

$$2V^{5+} + O^{2-} \rightarrow 2V^{4+} + \tfrac{1}{2}O_2 \uparrow$$

the V^{5+} ions occupy network forming positions in VO_5 trigonal bipyramidal structural units whereas V^{4+} ions form VO^{2+} complexes, which may act as modifiers and distort the glass network.

Recollecting the data on DTA studies, we have observed that the values of the glass transition temperature T_g and glass forming ability parameter $K_{gl}=(T_c-T_g)/(T_m-T_c)$ exhibited maxima at 0·6 mol% of vanadium oxide. Normally, the bond length, cross-link density and closeness of packing, are responsible for variation of these parameters. With increasing V_2O_5 concentration up to 0·6 mol%, the explanation of these results is that, with the increasing presence of V_2O_5 in the glass network, vanadium ions mostly are present as V^{4+} ions occupying modifying positions. Such an increase obviously suggests a high degree of disorder in the network of glass V_6.

The optical absorption spectrum of V_2O_5 doped glass exhibits two broad absorption bands at about 620 and 830 nm corresponding to $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2E$ transitions of VO^{2+} ions respectively;[46] there is a noticeable shifting of the meta-centres of these two bands towards lower wavelength side with a gradual increase in the intensity with increasing V_2O_5 concentration. V^{4+} ions have ad^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 $^2B_2$; and ^2E level splits into $^2A_1$ and $^2B_1$. Among these levels, the $^2B_2$ level will be the ground state. Thus for the vanadyl ions we can expect three bands (on the basis of energy level scheme for molecular orbitals of a VO^{2+} ion in a ligand field of C_{4v} symmetry provided by Bullhausen & Gray[31]) corresponding to the transitions $^2B_2 \rightarrow {}^2B_1$ ($\Delta_\perp$), $^2B_2 \rightarrow {}^2E$ ($\Delta_{||}$) and $^2B_2 \rightarrow {}^2A_1$. However, in the spectra of the present glasses, only the first two bands have been observed. The largest intensity and the half width of these bands for glass V_6, indicates that there is the largest concentration of VO^{2+} (vanadyl) ions in this glass. Such VO^{2+} ions are expected to participate in the depolymerisation of the glass network, creating more bonding defects and nonbridging oxygens (NBOs). As the concentration of vanadium oxide increases, the higher is the concentration of NBOs in the glass matrix. This leads to an increase in the degree of localisation of electrons there by increasing the donor centres in the glass matrix. The presence of larger concentration of these donor centres decreases the optical band gap and shifts the absorption edge towards higher wavelength side as observed.

The near invariance of the vibrational band of PO_4^{3-} group observed in the infrared spectra of the glasses with up to 0·6 mol% V_2O_5, suggests that the vanadium ions mostly occupy substitutional positions and participate in the formation of a layered structure with VO_5 trigonal bipyramids. With the gradual increase of V_2O_5 in the $PbO–MoO_3–P_2O_5$ glasses, a considerable decrease in the intensity of the bands due to P=O stretching vibrations and P–O–P symmetric stretching vibrations has been observed. Simultaneously an increase in the intensity of the bands due to P–O–P asymmetric bending vibrations has also been observed. These results indicate a growing disorder in the glass network with increasing V_2O_5 content.

The well-resolved hyperfine structure of the ESR spectra obtained for the glasses containing V_2O_5 (>0·6 mol%), is a typical of isolated V^{4+} ions in a ligand field of C_{4v} symmetry that are present as VO^{2+} species. The variations of the resolution and the line width of the ESR signal are obviously due to the variations in the concentration of V^{4+} ions and also due to structural and microstructural modifications, which can produce fluctuations in the degree of distortion or even of the coordination geometry of V^{4+} sites. The spectra indicate that VO^{2+} ions exist in the glass network in an octahedral sites with tetragonal compression since $g_{||} \leq g_\perp \leq g_e$;[46] further, an increase in the value of $\Delta g_{||}/\Delta g_\perp$ with increasing V_2O_5 concentration (Table 5), indicates tetragonal distortion around vanadyl ions increases with increasing concentration of V_2O_5. The broadening of the ESR signal with increasing concentration of V_2O_5 is apparently due to the pres-

ence of a larger concentration of V^{4+} ions and may also be due to exchange coupling between V^{3+} ions (if any) and V^{4+} ions.[47] The poor resolution of the ESR signal with low intensity in the spectra of the glasses containing low concentrations of V_2O_5 may be due to the presence of a low concentration of V^{4+} ions or a larger concentration of diamagnetic V^{5+} ions that occupy network-forming positions and also be due to an antiferromagnetic exchange interaction existing between V^{4+} ions (since V^{5+} ions are diamagnetic and there is no proof for the existence of considerable amounts of V^{3+} and V^{2+} ions) which may reduce the apparent concentration of V^{4+} ions.

5. Conclusions

A quantitative investigation of the spectroscopic properties, viz. optical absorption, ESR spectra and infrared spectra of $PbO–MoO_3–P_2O_5$ glasses containing different concentrations of V_2O_5 has been undertaken. The results indicate that with increasing V_2O_5 concentrations up to 0·6 mol%, there is an increasing presence of V_2O_5 in the glass network with vanadium mostly present as V^{4+} ions that occupy network modifying positions. Such an increase obviously suggests a high degree of disorder in the glass network.

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