

## RESEARCH ARTICLE

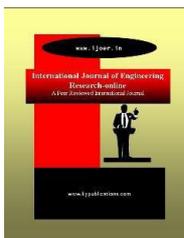
Spectroscopic features of vanadium ions in LiF–NaF–P<sub>2</sub>O<sub>5</sub> glassesK. NAVEEN KUMAR<sup>1</sup>, P. RAMESH BABU<sup>1</sup>, R. VIJAY<sup>1</sup>, K. SAMBASIVA RAO<sup>2\*</sup><sup>1</sup>Department of Physics, Acharya Nagarjuna University, Nagarjunanagar, A.P., India<sup>2</sup>Department of Physics, J.K.C. College, Guntur, A.P., India

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## ABSTRACT

LiF–NaF–P<sub>2</sub>O<sub>5</sub>: V<sub>2</sub>O<sub>5</sub> glasses with increasing concentration of NaF (in the range of 0–40mol% in steps of 10 mol %) were prepared. Spectroscopic properties viz., optical absorption, photoluminescence, IR and ESR spectra were carried out as a function of vanadium ion concentration. The optical absorption and ESR studies have revealed that vanadium ions do exist in both V<sup>4+</sup> and V<sup>5+</sup> states. The IR spectra have exhibited an additional band due to V–O–V bending vibrations in addition to the conventional bands due to phosphate groups. With the growing content of NaF in the glass matrix, the half width and the intensity of the peak is observed to increase. The distortion of the luminescence band observed in the lower energy side is attributed to the reabsorption by V<sup>3+</sup> ions if any in the glass network. The results have been further discussed quantitatively in the light of different valance states of vanadium ions with the aid of the data on spectroscopic properties.

Keywords: Spectroscopic properties; vanadium ions; LiF–NaF–P<sub>2</sub>O<sub>5</sub> glasses.

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## 1. INTRODUCTION

The mixed alkali effect in the glass materials has been the subject of study in the recent years. Many properties of glasses show nonlinear behavior of exhibiting a minimum or maximum, as a function of alkali content, if one of the alkali ions is gradually replaced by another alkali keeping total alkali content constant. This behavior is called mixed alkali effect. The general formula for mixed alkali fluorophosphates glass is  $y[x.AF + (1-x)BF] + (1-y)P_2O_5$ ; in this P<sub>2</sub>O<sub>5</sub> is the glass former, whereas A and B are alkalis. The extent of departure from linearity, the direction of variation (positive or negative) depends on the property examined and the glass system. The behavior of mixed alkali effect is independent of glass forming oxides. It is being observed in silicates, borates, phosphates, germinates, tellurites, boroaluminate, alumino silicates, borotellurate etc., glasses. It is also observed that properties related to cationic movement are more sensitive to mixed alkali effect. Further, the alkali oxide/fluoride mixed glasses are well known due to their potential applications as solid electrolytes.

Transition metal ions are very interesting ions to probe in the glass networks because of their broad radial distribution of outer d-orbital electron functions and their sensitive response to the surrounding actions [1-4]. Among various transition metal oxide glasses, the vanadium ions have attracted much interest in solid-state chemistry and material science  $V_2O_5$  is known to participate in the glass network with  $VO_5$ , pyramidal structural units. Several vanadate glasses show semiconducting behavior with the electrical conductivity of  $10^{-3}$  to  $10^{-5} (\Omega\text{-cm})^{-1}$ , which is known to be electron hopping between  $V^{4+}$  to  $V^{5+}$  ions, existing in the glass network. The content of vanadium in different forms in different valence states exist in the glass depends upon the quantitative properties of modifiers and glass formers, size of the ions in the glass structure, their field strength, 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.

A considerable number of spectroscopic and magnetic studies of vanadium ions in a variety of glass systems are also available [5-7]. The vanadium oxide structural groups are expected to mix easily in NaF–LiF– $P_2O_5$  network because some of the infrared vibrational bands of the structural groups of vanadyl ions lie in the same region as of the phosphate structural units and are expected to occupy a variety of sites with different crystal field strengths due to site variability. In this study we have attempted to have a comprehensive understanding over the topology and valence states of vanadium ions in mixed alkali fluoro phosphate glasses at the instance of variations in the relative proportions of NaF and LiF in the phosphate glass network.

## 2. Experimental

For the present study, a particular composition (40-x) LiF- x NaF- 59  $P_2O_5$ :1.0  $V_2O_5$  with five values of x ranging from 0 to 40 is chosen. The detailed compositions of the glasses (in mol%) are as follows:

$N_0$ : 40LiF– 60 $P_2O_5$  : 0  $V_2O_5$

$N_{10}$ : 30LiF–10NaF–59 $P_2O_5$ :1.0  $V_2O_5$

$N_{20}$ : 20LiF–20NaF–59 $P_2O_5$ :1.0  $V_2O_5$

$N_{30}$ : 10LiF–30NaF–59 $P_2O_5$ :1.0  $V_2O_5$

$N_{40}$ : 40NaF–59 $P_2O_5$ :1.0  $V_2O_5$

Appropriate amounts of analytical grade reagents of  $Li_2F$ ,  $NH_4H_2PO_4$ ,  $V_2O_5$ , and NaF powders, were thoroughly mixed in an agate mortar and melted at about 850 °C - 900 °C in an PID temperature controlled furnace for an hour until a bubble free transparent liquid was formed. The resultant bubble free melt was then poured in a brass mould and subsequently annealed about 200 °C.

The X- ray diffraction patterns of powdered glass samples were recorded on X'pert PRO analytical X-ray diffractometer fitted with copper target and nickel filter operated at 40 kV, 25 mA. The density (d) of the glasses was determined by the standard principle of Archimedi's using xylene (99.99 % pure) as the buoyant liquid. A direct reading balance (capacity 100 g, readability 0.1 mg) was used for weighing. The bulk glass was suspended on a very thin copper stand was set in the immersion liquid container and weighed in the liquid and air. The optical absorption spectra of the glasses were recorded using a JASCO Model V-670 Spectrophotometer in the wavelength range 300-1200 nm. The ESR spectra of the glasses were recorded at room temperature using commercial X-Band microwave spectrometer model JEOL JES-TES 100 of 100 kHz field modulation that works. FTIR spectra were recorded on a Bruker IFS 66 V – IR spectrophotometer with a resolution of  $0.1 \text{ cm}^{-1}$  in the range  $400\text{-}2000 \text{ cm}^{-1}$  using potassium bromide pellets (300 mg) containing pulverized sample (1.5 mg). The photoluminescence spectra of glasses were recorded on Photon Technology International fluorescence spectrophotometer in UV and NIR regions with a monochromator and photomultiplier tube for detecting the luminescence response in the appropriate wavelength regions.

## 3. Results

### 3.1 Physical Parameters

From the measured values of density d and calculated average molecular weight  $\overline{M}$ , various physical parameters such as vanadium ion concentration  $N_i$  and mean vanadium ion separation  $r_i$  of these glasses are evaluated using the conventional formulae and are presented in Table 3.1.

Table 3.1: Physical Parameters of LiF–NaF–P<sub>2</sub>O<sub>5</sub> glasses mixed with various concentrations of V<sub>2</sub>O<sub>5</sub>.

Sample	Conc. Ti <sub>2</sub> O <sub>3</sub> (mol%)	Avg.Mol. wt. $\bar{M}$	Density $\rho$ (g/cm <sup>3</sup> ) ( $\pm 0.001$ )	Field Strength ( x 10 <sup>16</sup> cm <sup>-2</sup> )	Conc. Vanadium ions N <sub>i</sub> (x10 <sup>22</sup> ions/cm <sup>3</sup> ) ( $\pm 0.01$ )	Inter ionic distance of Vanadium ions R <sub>i</sub> (Å) ( $\pm 0.001$ )	Polaron radius R <sub>p</sub> (Å) ( $\pm 0.001$ )
N <sub>0</sub>	0	102.35	2.466	1.83	1.45	4.09	1.65
N <sub>40</sub>	4	100.75	2.474	1.86	1.48	4.07	1.64
N <sub>30</sub>	3	99.15	2.482	1.88	1.51	4.05	1.63
N <sub>20</sub>	2	97.54	2.490	1.90	1.54	4.02	1.62
N <sub>10</sub>	1	95.94	2.497	1.93	1.57	3.99	1.61

XRD patterns of some of the prepared samples are shown in Fig. 3.1; the pattern did not indicate any sharp Bragg peaks confirming the amorphous nature of samples.

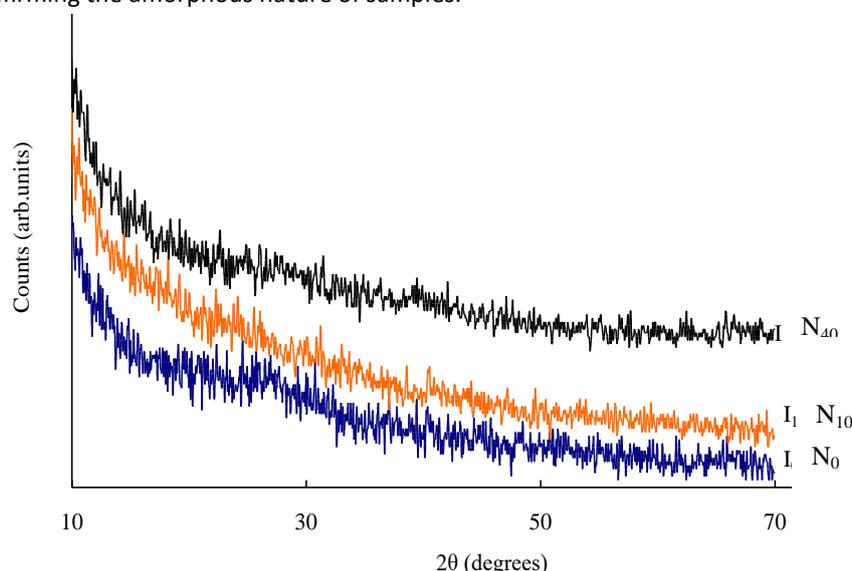


Fig. 3.1 XRD patterns of NaF – LiF – P<sub>2</sub>O<sub>5</sub> : V<sub>2</sub>O<sub>5</sub> glasses.

The infrared transmission spectra of LiF–NaF–P<sub>2</sub>O<sub>5</sub>: V<sub>2</sub>O<sub>5</sub> glasses (Fig. 3.2) exhibit vibrational bands around 1282 cm<sup>-1</sup> (band due to anti-symmetrical vibrations of PO<sub>2</sub><sup>-</sup> groups, this region may also consists of bands due to P=O stretching vibrations), 1077 cm<sup>-1</sup> (a normal vibrational mode of symmetrical stretching vibrations of PO<sub>2</sub><sup>-</sup> in PO<sub>4</sub><sup>3-</sup> groups), at 878 cm<sup>-1</sup> due to P-O-P asymmetric vibrations [8-11]. Another band due to P-O-P symmetric stretching vibrations also located around 780 cm<sup>-1</sup> [8-12]. With the gradual increase of NaF with simultaneous decrease of LiF in LiF–NaF–P<sub>2</sub>O<sub>5</sub>: V<sub>2</sub>O<sub>5</sub> glasses, the following changes have been 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 wavenumber with increasing intensity, iii) a considerable decrease in the intensity of PO<sub>4</sub><sup>3-</sup> band with a shift towards lower wavenumber is observed; further in the spectrum of V<sub>2</sub>O<sub>5</sub> doped glass(N<sub>10</sub>), an intense absorption band with a meta-center at about 780 cm<sup>-1</sup> related to V-O-V chains and a weak band at about 598 cm<sup>-1</sup> corresponding to bending vibrations of the vanadium ions[13] have also been observed. In the region of symmetric stretching vibrations of PO<sub>4</sub><sup>3-</sup> units, band due to vibrations of isolated V=O groups in the VO<sub>5</sub> trigonal bipyramids is also expected [14]. A summary of the data on the positions of various bands in the IR spectra of LiF–NaF–P<sub>2</sub>O<sub>5</sub>:V<sub>2</sub>O<sub>5</sub> glasses are presented in the Table 3.2.

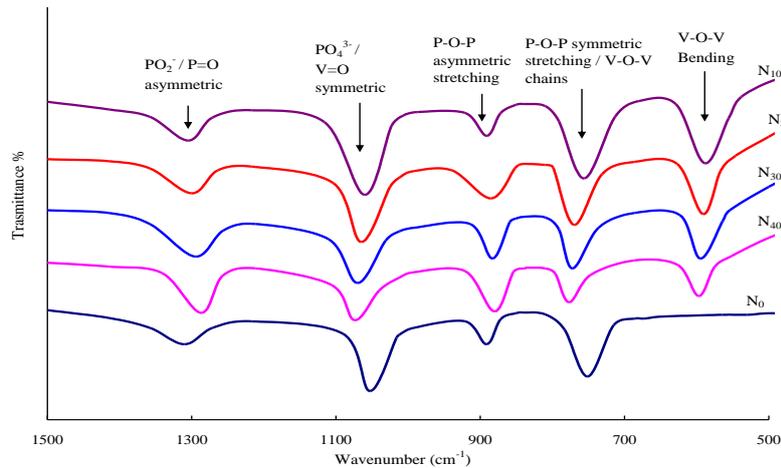


Fig. 3.2 IR spectra of NaF – LiF – P<sub>2</sub>O<sub>5</sub> : V<sub>2</sub>O<sub>5</sub> glasses

Table 3.2: Assignment of FTIR bands (cm<sup>-1</sup>) with a probable error of ± 0.1cm<sup>-1</sup> of LiF–NaF–P<sub>2</sub>O<sub>5</sub>: V<sub>2</sub>O<sub>5</sub> glasses

Sample	PO <sub>2</sub> <sup>-</sup> / P=O asymmetric	PO <sub>4</sub> <sup>3-</sup> / V=O Symmetric groups	P- O - P symmetric Stretching	P- O - P asymmetric Stretching / V-O-V chains	V-O-V bending
N <sub>0</sub>	1310	1052	893	750	---
N <sub>10</sub>	1305	1060	890	756	588
N <sub>20</sub>	1300.4	1065	885	770	592
N <sub>30</sub>	1295	1070	882.9	772.1	595.8
N <sub>40</sub>	1287	1074.3	880	777.1	597.9

Fig.3.3 represents the optical absorption spectra of LiF–NaF–P<sub>2</sub>O<sub>5</sub>: V<sub>2</sub>O<sub>5</sub> glasses recorded at room temperature in the wavelength region 400-1200 nm. The absorption edge observed at 467 nm for N<sub>10</sub> glass is observed to shift towards higher wavelength side with increase in the content of NaF. The spectrum of glass N<sub>10</sub> has exhibited two broad absorption bands at 695 and 880 nm corresponding to <sup>2</sup>B<sub>2</sub> → <sup>2</sup>B<sub>1</sub> and <sup>2</sup>B<sub>2</sub> → <sup>2</sup>E transitions of VO<sup>2+</sup>

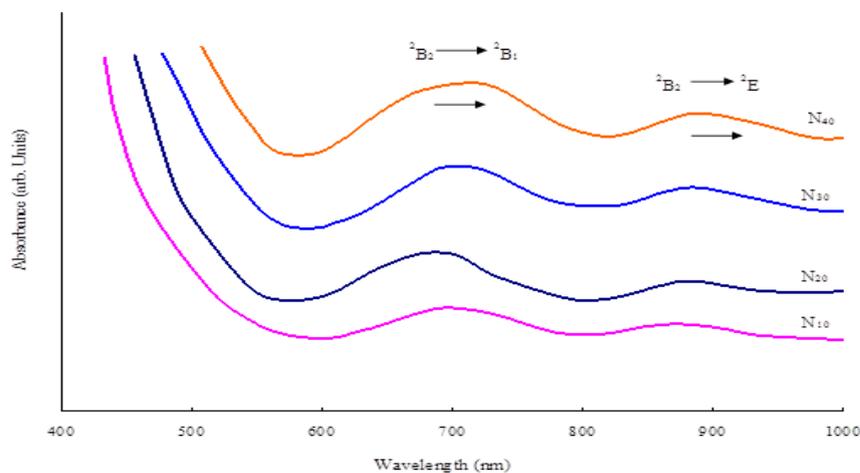


Fig. 3.3 Optical absorption spectra of NaF – LiF – P<sub>2</sub>O<sub>5</sub> : V<sub>2</sub>O<sub>5</sub>

ions [15]; with increase in the concentration of V<sub>2</sub>O<sub>5</sub>, the half width and peak height of these bands are observed to increase. From the observed absorption edges, we have evaluated the optical band gaps (E<sub>0</sub>) of these glasses by drawing Urbach plots (Fig. 3.4) between (αħω)<sup>1/2</sup> and ħω as per the following equation:

$$\alpha(\omega) \hbar\omega = c (\hbar\omega - E_0)^2 \tag{1}$$

Fig.3.4 represents the Urbach plots of all these glasses in which a considerable part of each curve is observed to be linear. The values of optical band gap (E<sub>0</sub>) obtained from the extrapolation of these curves are presented in table 3.3. The value of E<sub>0</sub> is found to decrease with increase in the concentration of NaF in the glass matrix (Table 3.3)

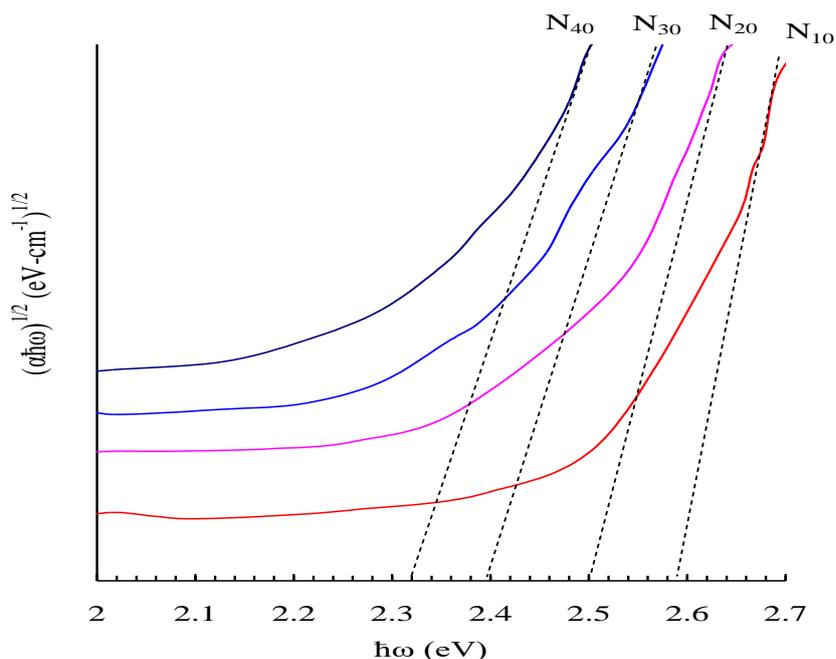


Fig. 3.4 Urbach plots for evaluating optical band gap of NaF – LiF – P<sub>2</sub>O<sub>5</sub> : V<sub>2</sub>O<sub>5</sub> glasses

Table 3.4: Summary of data on optical absorptions data of LiF–NaF–P<sub>2</sub>O<sub>5</sub>: V<sub>2</sub>O<sub>5</sub> glasses

Sample	λ <sub>c</sub> ( nm) (±0.1)	Band Positions (nm) (±0.1)		E <sub>0</sub> (eV) (±0.01)
		<sup>2</sup> B <sub>2</sub> → <sup>2</sup> B <sub>1</sub>	<sup>2</sup> B <sub>2</sub> → <sup>2</sup> E <sub>1</sub>	
T <sub>10</sub>	467	695	880	2.60
T <sub>20</sub>	480	700	884	2.49
T <sub>30</sub>	492	705	890	2.38
T <sub>40</sub>	506	709	893	2.32

Fig.3.5 shows the photoluminescence spectra of LiF–NaF–P<sub>2</sub>O<sub>5</sub>: V<sub>2</sub>O<sub>5</sub> glasses recorded at room temperature with the excitation wavelength of 690nm. The spectrum of glass N<sub>10</sub> exhibits a broad emission band in the region 740-810 nm; this band is identified due to <sup>2</sup>E → <sup>2</sup>T<sub>2</sub> transition of vanadyl ion, the band exhibits a slight asymmetry in the higher wavelength region. With the growing content of NaF in the glass matrix, the half width and the intensity of the peak is observed to increase.

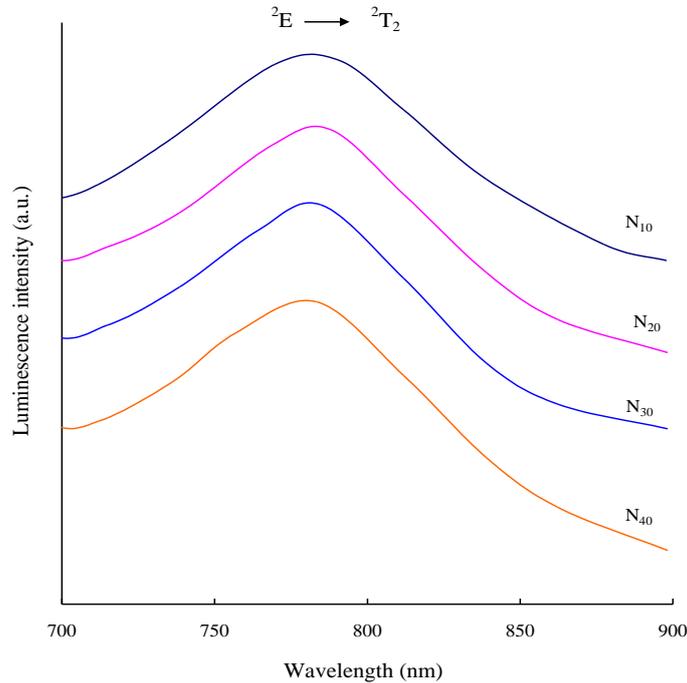


Fig. 3.5 Photoluminescence spectra of NaF – LiF – P<sub>2</sub>O<sub>5</sub> : V<sub>2</sub>O<sub>5</sub> glasses recorded at room temperature ( $\lambda_{exc} = 690$  nm)

The ESR spectra, recorded at room temperature for LiF–NaF–P<sub>2</sub>O<sub>5</sub>: V<sub>2</sub>O<sub>5</sub> glasses under investigation are shown in Fig. 3.6; spectra are observed to be complex made up of resolved hyperfine components arising from unpaired 3d<sup>1</sup> electron with <sup>51</sup>V isotope whose spin is 7/2. As the concentration of NaF is increased, an increasing degree of resolution and the intensity of signal have been observed. The values of  $g_{||}$  and  $g_{\perp}$  (obtained from these spectra) along with the other pertinent data are furnished in Table 3.4. Similar to fluoro borate glass network, the phosphate glass network containing alkali-fluorides like LiF/NaF may consist of P(O, F)<sub>4</sub> or PO<sub>3</sub>F or PO<sub>2</sub>F<sub>2</sub>.

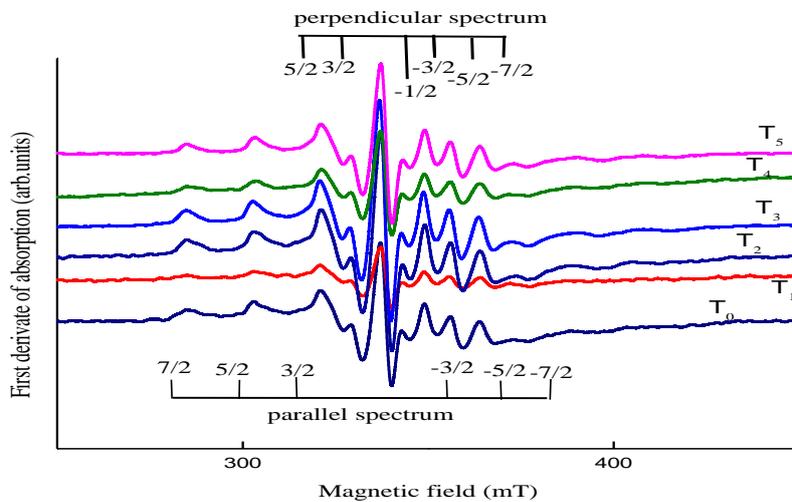


Fig. 3.6 ESR spectra of NaF – LiF – P<sub>2</sub>O<sub>5</sub> : V<sub>2</sub>O<sub>5</sub> glasses recorded at room temperature

Table3. 4: Data on ESR parameters of LiF–NaF–P<sub>2</sub>O<sub>5</sub>: V<sub>2</sub>O<sub>5</sub> glasses

Sample	$g_{  }$ (±0.001)	$g_{\perp}$ (±0.001)	$\Delta g_{  }/\Delta g_{\perp}$ (±0.01)
N <sub>10</sub>	1.912	1.998	21.00
N <sub>20</sub>	1.914	1.996	14.02
N <sub>30</sub>	1.915	1.995	11.96
N <sub>40</sub>	1.917	1.994	10.28

4. Discussion

P<sub>2</sub>O<sub>5</sub> is a well-known network former with PO<sub>4</sub> structural units with one of the four oxygen atoms in PO<sub>4</sub> tetrahedron is doubly bounded to the phosphorus atom with the substantial π-bond character to account for pentavalency of phosphorous [16]. The PO<sub>4</sub> tetrahedrons 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 non bridging oxygen atoms of each PO<sub>4</sub> tetrahedron. In general the P-O-P bond between PO<sub>4</sub> tetrahedral is much stronger than the cross bond between chains via the metal cations [17]. The alkali fluorides viz., LiF, NaF act as a modifier (normally the fluoride’s of these oxides break the local symmetry while cations occupy interstitial positions) and introduces co-ordinated defects known as dangling bonds along with non bridging oxygen ions. LiF and NaF are conventional modifiers and enter the glass network, either by rupturing or by breaking up P-O-P bonds (normally the fluoride ions break the local symmetry while Li<sup>+</sup> and Na<sup>+</sup> ions occupy interstitial positions) and introduce coordinated defects known as dangling bonds along with non-bridging oxygen ions. Similar to fluoro borate glass network, the phosphate glass network containing alkali-fluorides like LiF/NaF may consist of P(O, F)<sub>4</sub> or PO<sub>3</sub>F or PO<sub>2</sub>F<sub>2</sub> or units as shown in Fig. 3.7.

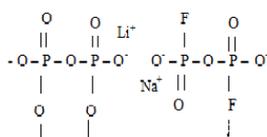
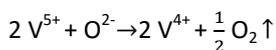


Fig. 3.7 A schematic illustration of alkali fluoro phosphate glasses

Vanadium ions are expected to exist mainly in V<sup>5+</sup> states in the present LiF–NaF–P<sub>2</sub>O<sub>5</sub>: V<sub>2</sub>O<sub>5</sub> glass network. However, during the melting of the glasses at higher temperature there is every possibility for the following redox equilibrium to take place:



the V<sup>5+</sup> ions take part network forming positions with VO<sub>5</sub> trigonal bipyramidal structural units whereas the V<sup>4+</sup> ions from VO<sup>2+</sup> complexes, may act as modifiers and distort the glass network similar to alkali fluorides.

The vibrational band of PO<sup>3-</sup><sub>4</sub> group/ V=O groups observed in the IR spectra in the region 1050-1070 cm<sup>-1</sup> in these glasses, suggests the presence of vanadium ions mostly in the substitutional positions and participate in the formation of layered structure with VO<sub>5</sub> trigonal bipyramids. With the gradual increase in the content of NaF in the LiF–NaF–P<sub>2</sub>O<sub>5</sub> 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 point out a growing disorder in the glass network with increasing presence of NaF.

The optical absorption spectrum of V<sub>2</sub>O<sub>5</sub> doped glass exhibited to broad absorption bands corresponding to <sup>2</sup>B<sub>2</sub>→<sup>2</sup>B<sub>1</sub> and <sup>2</sup>B<sub>2</sub>→<sup>2</sup>E transitions of VO<sup>2+</sup> ions respectively [15]; there is a noticeable shifting of the meta centers of these two bands towards higher wavelength side with a gradual hike in the intensity with increase in the concentration of NaF. V<sup>4+</sup> ion belongs to d1 configuration with <sup>2</sup>D as the ground

state. 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 three  ${}^2B_2$  (viz.  $|xy$ ,  $|yz$  and  $|zx$ ) states and  ${}^2E$  excited state splits into  $A_1 - 3z^2 - r^2 >$  and  $B_1x^2 - y^2 >$  (ground state). Among these, the  ${}^2B_2$  will be the ground state. Thus for the vanadyl ions we can expect 3 bands (on the basis of energy level scheme for molecular orbitals of  $VO^{2+}$  ion in a ligand field of  $C_{4v}$  symmetry provided by Bullhausen and Gray[15] corresponding to the transitions

${}^2B_2 \rightarrow {}^2B_1(\Delta g_{\perp})$ ,  ${}^2B_2 \rightarrow {}^2E(\Delta g_{||})$  and  ${}^2B_2 \rightarrow {}^2A_1$ . However, in the spectra of the present glasses, only the first two bands towards higher concentration of NaF in the glass matrix. This observation clearly suggests the presence of larger concentration of vanadyl ions in the glasses containing higher concentrations of NaF.

The optical activation energy associated with the both absorption bands is decreased with increase in the concentration of NaF in the glass samples; this is clearly a characteristic signal of inter valency transfer or a polaronic type of absorption. To be more specific, the associated electrons are still trapped at shallow sites within the main band gap and yet have smaller wave-function radii. In terms of polaronic perception, this kind of situation is only possible if the local potential fluctuation is small as compared to the transfer integral,  $J$ . A small overlap between electronic wave function (corresponding to adjacent sites) due to strong disorder is contributive to polaron formation. So from the polaronic viewpoint, the electron delivered by the impurity atom at the  $V^{5+}$  site converts this into a lower valence state  $V^{4+}$ , and at the next stage, the trapped electron at this  $V^{5+}$  site is transferred to the neighboring new  $V^{5+}$  site by absorbing a photon energy. Thus the optical absorption in the glass samples is dominated by polaronic transfer between the  $V^{4+}$  and  $V^{5+}$  species depending upon the state of coloration, i.e., when the samples turn into blue coloration [18,19].

With the increase in concentration of NaF at the expense of LiF in the glass network, a large number of donor centers are created (obviously due to larger ionic size of Na ion when compared with Li ion) and subsequently, the excited states of localized electrons originally trapped on  $V^{4+}$  sites begin to overlap with the empty 3d states on the neighboring  $V^{5+}$  sites, and as a result, the impurity or polaron band becomes more extended into main band gap. This new polaronic development might have shifted the absorption edge to the lower energy (Table 3) which leads up to a significant shrinkage in the band gap as the concentration of NaF in increased.

Excitation of LiF–NaF– $P_2O_5$ :  $V_2O_5$  glass samples with the wavelength corresponding to  ${}^2B_2 \rightarrow {}^2B_1$ , resulted a broad emission band as shown in Fig. 3.5. Since the wavelength of this band is close to the maximum of the band  ${}^2B_2 \rightarrow {}^2E_1$ , we attribute this band as the  ${}^2E_2 \rightarrow {}^2T_2$  transition of  $V^{4+}$  ions; the emission band is relatively broad and structureless. With increase in the concentration of NaF, the intensity of the peak is observed to increase with a red shift. The shift of this PL peak, the shape and the structured nature of the PL emission band are a signature of shallow levels with an electron-phonon coupling. The distortion of the luminescence band in the lower energy side is probably due to the reabsorption by  $V^{3+}$  ions if any in the glass network[20].

The well-resolved hyperfine structure of the ESR spectra obtained for the glasses containing  $V_2O_5$  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 ESR signal are obviously due to the variation in the concentration of  $V^{4+}$  ions and also due to structural and micro structural modifications due to variations in the relative concentration of alkali fluorides, which can produce fluctuation of 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 site symmetry with tetragonal compression since  $g_{||} \leq g_{\perp} \leq g_e$  [21]; further, a decrease in the value of  $\Delta g_{||} / \Delta g_{\perp}$  with increase in the concentration of NaF (Table 3.4), indicates an increase in the tetragonal distortion around vanadyl ions. The broadening of ESR signal with the concentration of NaF indicates either the presence of the larger concentration of  $V^{4+}$  ions or the exchange coupling between  $V^{3+}$  ions (if any) and  $V^{4+}$  ions[22]. The low degree of resolution of the ESR signal with low intensity in the spectra of

the glasses containing low concentration of NaF indicate either the presence of low concentration of  $V^{4+}$  ions are larger concentration of diamagnetic  $V^{5+}$  ions that take network-forming positions and also due to antiferromagnetic exchange interaction existing between  $V^{4+}$  ions (since  $V^{5+}$  ion is a diamagnetic and there is no proof for existence of considerable amounts of  $V^{3+}$  and  $V^{2+}$  ions) which may reduce the apparent concentration of  $V^{4+}$  ions.

## 5. conclusions

$LiF-NaF-P_2O_5: V_2O_5$  glasses with relative variations in the concentration of LiF and NaF (ranging from 0 to 40 mol%) were prepared. Spectroscopic studies *viz.*, optical absorption, photoluminescence, IR and ESR have been investigated. Optical absorption, ESR have indicated that vanadium ions exist in  $V^{4+}$  state in addition to  $V^{5+}$  state. The IR spectra have exhibited an additional band due to V-O-V bending vibrations in addition to the conventional bands due to phosphate groups; from these observations, it is concluded that there is a growing degree of disorder in the glass network with increase in the concentration of NaF at the expense of LiF in the glass matrix.

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