Mixed alkali effect on borosilicate glass structure with vanadyl ion as spin probe

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Abstract
Mixed alkali borosilicate glasses doped with 2% vanadium oxide were synthesized by conventional melt-quench method. The Micro structure of the materials was analysed using XRD, SEM and EDX spectrum. Optical nature of glasses was studied by computing optical bandgaps with absorption spectral data. Covalent nature of glasses was estimated correlating optical bandgap energy with EPR spectral data. The metallization criterion of glasses was evaluated from the physical parameters. FTIR and Raman spectral techniques were used to identify the structural groups of the borates and silicates that are formed with addition of modifiers. Emission spectra were recorded at excitation wavelength of 350 nm and their thermal nature was also studied using TGA/DTA techniques.

1. Introduction

The number of NBO (non-bridging oxygen) and thus the glass materials properties are comfortably modified by the addition of alkali oxides or by doping transition metals. Complex structure in borosilicate glass influences the local environment around alkali ions [1]. So a structural study is necessary to elucidate the properties of binary alkali borosilicate glass. The structure of any material depends on the coordination number and bond nature. Transition metals occupy interstitial sites, so they are good probes to find the structure of the glass.

Transition metals have multiple potential oxidation states which directly influence the electrochemical properties of materials. Vanadium ions (Atomic number - 23) exist in four oxidation states divalent, trivalent, tetravalent and pentavalent. They act as magnificent probe ions due to their large radial distribution of d - orbital electron wave function, which affects the spin–orbit coupling parameters [2]. Hence, materials contain Vanadium oxide exhibits fascinating electrochemical, photochemical, catalytical and spectroscopic properties [3, 4]. It also shows excellent broad band luminescent properties in near IR. So Vanadium has many applications in photonics such as smart glass etc [5, 6]. Vanadium doped glasses are also capable to transform UV into visible light [7]. The dependence of conductive properties on temperature of vanadium materials is used to design excellent compact electronic data storage mechanism and also to construct nanobots. Electron hopping between vanadate ions increases the number of NBO’s and so electrical conductivity of material is increased [8]. It is also used to recharge the storage batteries at grid levels due to it’s various oxidation states.

Vanadium ions on the structure of borosilicate glasses has got a lot of significance because of their distinct applications in luminescence, conductivity, high absorption, change in activation energy and nuclear waste storage and elastic properties [9–12].

From the literature studies it is obvious to say that there may be a number of spectroscopic studies available on vanadium dopant glasses, but very limited studies are available for binary alkali borosilicate glass [13–15]. Hence in this present work we have attempted to investigate in detail, how vanadium ions manipulate the spectroscopic properties of mixed alkali Borosilicate glass by systematic variation of the alkali oxides Na2O/K2O ratio.
2. Experimental preparation of glass samples

Analar grade chemicals (Loba) were precisely weighted proportional to their mol% to prepare 15 gm of glass sample. The details of the glass composition are shown in Table 1. The chemicals were ground and the obtained fine powder was taken in a Silica crucible and melted at 1040°C–1060°C for an hour in a muffle furnace. After getting bubble free melt it was stirred and was poured on a flat brass plate at room temperature. Now these quenched glasses are immediately kept in a furnace at 450°C for 3 h to avoid cracks. Now these annealed glasses were optically polished for characterisation.

2.1. Characterization of glass samples

The disorder in structure of glass was reassured by XRD using an XpertPRO analytical x-ray diffractometer with Cu Kα radiation. The surface transparency was observed with scanning electron microscope pictures (FE - SEM; ZEISS of resolution 0.8 nm). Elements in glass composition were identified by dispersive x-ray spectroscopy (EDX). With Perkin Elmer lambda 950 UV–vis - NIR spectrophotometer characteristic light absorption spectra of glasses were recorded in wavelength range 200-1300 nm. FTIR and Raman spectral techniques identifies the structural groups of borate and silicates formed with the addition of modifiers. For Detection of paramagnetic species, EPR spectra were recorded at room temperature in X-band frequencies (9 GHz) with a field modulation of 100 KHz using EPR spectrometer (JEOL: JES-FA200). The photoluminescence spectra of glass samples were recorded using JY Fluorolog-3-11 fluorimeter.

3. Results and discussions

3.1. Physical properties

Physical parameters of the glass like molecular weight of composition (M), molar volume (V_m), vanadyl ion concentration (N_i), mean Vanadyl ion separation (r_i), Polaron radius (r_p), field strength are evaluated using conventional formulae [16, 17]. The values obtained are presented in Table 2.

By the replacement of Na⁺ ions with K⁺ ions molar volume decreases from V_5 to V_25. It was observed that with the reduction in molar volume the number of transition metal ions per unit volume (TM ion concentration, N_i) increases.
Further, the reduction in molar volume reduces theoretically, the average separation between successive transition metal ions ($r_i$) and polaron radius. So, the Field strength between transition metal ions from $V_5$ to $V_{25}$ glass increases.

Refractive index at band edge, molar refraction, polarizability and Metallization criterion were computed using the optical bandgap, which are included in table 2. These parameters are estimated with standard formulae [18, 19]. It is found that $Rm/Vm$ value is a little bit larger for $V_{10}$ glass than other studied glasses. This shows $V_{10}$ glass has less covalent nature or more metallic nature when compared to the other glasses studied.

3.2. Micro structure analysis (SEM, EDX & XRD)

In this section SEM, EDX for $V_{20}$ glass and XRD for all glasses studied are enclosed. These are given in figures 1–3 respectively.

The scanning electron microscope pictures of the undoped and vanadyl ion doped glasses are shown in figure 1. The image clearly shows the texture of glass changing due to the doped vanadyl ions. Similar observations are drawn for remaining glasses too.

The elements present in the glass composition are identified by EDX spectrum and their atomic % and weight % data is shown graphically in figure 2. Similar like observations are made with remaining glasses too.

The x-ray diffraction pattern of studied glasses are shown in figure 3. The x-ray diffraction of vanadyl doped glasses have no sharp peaks only a diffused band is observed. This is a feature of long range disorder which ensures the non-crystalline nature of the studied material.
3.3. Thermal stability of the glass

Thermo Gravimetric Analysis (TGA) and Differential thermal analysis (DTA) were recorded for the V10 glass given in figure 4. It shows the endothermic peaks of glass transition temperature ($T_g$), melting temperature ($T_m$) and exothermic peak of crystallization temperatures ($T_{c1}, T_{c2}$).

Mass degradation with temperature of a material is estimated from TGA curve. Beyond 563 °C mass loss was more. The glass transition temperature ($T_g$), the first crystalline temperature ($T_{c1}$) and the second crystalline temperature ($T_{c2}$) for V10 glass were 495 °C, 605 °C and 713 °C respectively from the DTA curve. Elastic nature of glass depends on the super cooled temperature $DT = T_{c1} - T_g$. For the glass V10, the super cooled temperature is 110 °C. The high $DT$ of the studied glasses indicates their good ductile nature, so they could be used as good sealants [20].

3.4. Optical absorption study

Optical absorption spectra were used to get information about bandgaps and defect levels. UV absorption spectrum of semiconductor materials is associated with the transitions of energy greater than bandgap and Visible-IR spectra collects the data related to lesser energy transitions. So we recorded absorption spectra in between 200 nm–1200 nm transitions for all the glasses.
In Optical absorption spectra of all investigating glasses, two bands at wavelengths around 600 nm and 1020 nm were observed and were assigned to the transitions $^2B_2g \rightarrow ^2B_1g$, $^2B_2g \rightarrow ^2E_g$, (figure 5) the same characteristics transitions of $V^{4+}$ were reported in earlier studies by a number of researchers [21–26].

The ligand field is not symmetrical about the central transition metal cation ($V^{4+}$) since for $E_g$ orbitals lobes are exactly in the approaching direction of ligands so they experiences more columbic force than the $T_{2g}$ orbitals. So, the distance of ligands along $z$-axis is slightly different compared with the other ligands in this octahedron structure and was thus distorted tetragonally. The ground state energy level of the vanadyl complexes is the 3d$^1$ electron in $d_{xy}$—orbital which is denoted as $^3B_{2g}$. Energy level diagram of 3d$^1$ - electron is shown in figure 6 with the reported transitions in the studied glasses.

3.4.1. Optical band gap

The applications of materials in optoelectronics are decided by their energy gap ($E_g$). Optical absorption coefficient $\alpha$ depends on joint density of valence, conduction and impure energy states. In direct bandgap transitions, charge carriers energy and momentum both are conserved. These allowed vertical transitions are represented by a linear region of Tauc plot obeying the below relation (1).

$$ (\alpha h\nu)^2 = A(h\nu - E_{direct}). $$

(1)

The indirect bandgap oblique collisions are associated with phonons for the conservation of momentum. In our studied glasses $E_{indirect} < E_{direct}$ indicates less energy is enough for phonon assisted oblique transition than vertical allowed transition. Here $\alpha$ depends on absorption coefficients of both photon and phonon followed by the relation (2).

$$ (\alpha h\nu)^{1/2} = A(h\nu - E_{indirect}). $$

(2)
The conduction and valence band edges are not well defined with the addition of modifiers and impurities like transition metals to the glass. Impurities bandtails penetrate into the bandgap region. The transitions between bandtails lead to Urbach energy $\Delta E$. The absorption coefficient depends on density of energy states at bandedge and increases exponentially with energy, according to relation $(3)$ [27, 28].

$$\alpha(\nu) = \alpha(\nu_0) \exp \frac{h\nu}{\Delta E}. \hspace{1cm} (3)$$

Larger are the Defect level energies; smaller is the optical band gap. The calculated bandgaps and Urbach energies of studied glasses are shown in Table 3. It is observed that $V_{10}$ glass has less bandgap and more Urbach energy.

### 3.5. Emission spectra

The fluorescence spectra of all vanadyl doped glasses are shown in figure 7, at the excitation wavelength 350 nm. A broad Emission band was observed ranging from 420 to 650 nm with a maximum around 540 nm. Hence these glasses could be used as sensors to detect ultraviolet radiation yielding green light. The emission wavelength shift is in reverse trend of the cut-off wavelengths of the glass series. These emission centres were because of the oxygen vacancies or interstitial defects present in glasses [2, 3, 29].

### 3.6. EPR study

The EPR spectral plots of the first derivative of absorbance versus the magnetic field intensity (mT) in X-band frequency (9.32 GHz) at room temperature is shown in figure 8. In EPR spectra 8 perpendicular components and 6 parallel components are clearly seen, the other 2 parallel components are masked by the strong perpendicular components.

The calculated parameters from EPR spectra are shown in table 4.

The anisotropic environment around the metal $d$-electron affects the spin–Hamiltonian parameters. For the studied glasses the spin Hamiltonian parameters vary as $g_L < g_\perp < g_e$ ($g_e = 2.0023$) and $A_L > A_\perp$. This trend in spin—Hamiltonian parameters suggests that the interstitial site of $V^{4+}$ ion in the studied glasses is tetragonally compressed octahedron with $V^{4+}$ as central metal ion. This tetragonal structure has $C_{4v}$ symmetry and the ground state is $d_{x^2}$ orbital. [23–26, 29, 30]. Ligands aligned along $z$-direction experience more columbic force than other ligands. This leads to a shrink in $V = O$ bond length along $z$-direction and is compressed tetragonally. In present glasses the tetragonality measure $\frac{(g_e - g_L)}{(g_e - g_\perp)}$ slightly varies with the alkalis concentration.

### Table 3. Absorption wavelengths & Optical bandgaps of Vanadyl doped SiO$_2$- R$_2$O$_3$- Na$_2$O-K$_2$O Glasses.

| Sample Code | Transition $^2B_{2g} \rightarrow {}^2B_{1g}$ | Trans. $^2B_{2g} \rightarrow {}^2E_g$ | cut-off wavelength (nm) | direct band-gap (eV) | indirect band-gap (eV) | Urbach energy (eV) |
|-------------|-------------------------------------------|---------------------------------|------------------------|------------------|-------------------|-------------------|
| $V_5$       | 582                                       | 1055                            | 394                    | 3.22             | 3.16              | 0.15              |
| $V_{10}$    | 587                                       | 970                             | 416                    | 3.10             | 3.00              | 0.24              |
| $V_{15}$    | 600                                       | 1030                            | 407                    | 3.13             | 3.04              | 0.11              |
| $V_{20}$    | 612                                       | 1042                            | 406                    | 3.14             | 3.04              | 0.21              |
| $V_{25}$    | 692                                       | 1050                            | 399                    | 3.19             | 3.10              | 0.20              |

Figure 6. Energy level diagram of 3$d^1$ electron of vanadyl ion tetragonal compression of octahedral site.
More Z-in distortion results more localization of orbitals at vanadium atom. Tetragonality measure is more for V10 glass implying this glass is less covalent in nature. Metallization criterion parameter of V10 glass from table 3 also informs the same.

Fermi contact terms $\kappa$ and the dipolar interaction parameter $P$ are used to assess the extent of distortion. Isotropic distortion was theoretically calculated as $P = g_e g_N \beta_N r^{-3}$ and from EPR and optical absorption experimental data it was computed as

$$ P = \frac{7(A\parallel - A\perp)}{(6 + (3/2)(\lambda/\Delta||))}. $$

$\Delta||$ is the electron transition energy from $d_{xy}$ orbital to $d_{x^2-y^2}$ orbital corresponding to $^2B_{2g} \rightarrow ^2B_{1g}$ transition. In VO$(H_2O)^{2+}$ the bond between vanadium and hydroxyl ions is purely ionic, and the value of $P$ is $160 \times 10^{-4}$ cm$^{-1}$. The lower values of ‘$P$’ for the studied glasses than for the pure ionic vanadium complex indicates the

**Figure 7.** Emission spectra of xNa$_2$O-(30-2x)K$_2$O-38SiO$_2$-30B$_2$O$_3$.2V$_2$O$_5$ glasses at excitation wavelength 350 nm.

**Figure 8.** EPR spectra of xNa$_2$O-(30-2x)K$_2$O-38SiO$_2$-30B$_2$O$_3$.2V$_2$O$_5$ glasses in X-band frequency at room temperature.
Table 4. Spin–Hamiltonian Hyperfine coupling parameters, Tetragonality & Covalency ratios of xNa2O-(30-x)K2O-38SiO2-30B2O3 Glasses.

| Glass code | g|| | A|| (10⁻⁴ cm⁻¹) | g⊥ | A⊥ (10⁻⁴ cm⁻¹) | P | κ | β² | 1-α² | 1-γ² | Δg||/Δg⊥ | P’κ | A|| (10⁻⁴ cm⁻¹) | A⊥ (10⁻³ cm⁻¹) |
|------------|----|----------------|----|----------------|---|---|---|---|---|---|-------|---|-------|---|----------------|
| V₅         | 1.9217 | 174.8 | 1.987 | 50.75 | -145.3 | 0.60 | 0.909 | 0.23 | 0.70 | 5.08 | 86.74 | 88.14 | 35.99 |
| V₁₀        | 1.9216 | 176.9 | 1.991 | 63.6 | -132.7 | 0.73 | 0.907 | 0.24 | 0.76 | 6.72 | 96.80 | 80.13 | 33.20 |
| V₁₅        | 1.9254 | 175.7 | 1.984 | 54.176 | -142.3 | 0.63 | 0.914 | 0.29 | 0.64 | 4.08 | 89.31 | 86.42 | 35.13 |
| V₂₀        | 1.9215 | 176.0 | 1.982 | 61.02 | -134.6 | 0.70 | 0.910 | 0.27 | 0.60 | 3.86 | 93.89 | 82.11 | 32.86 |
| V₂₅        | 1.9235 | 175.0 | 1.986 | 63.32 | -130.8 | 0.73 | 0.910 | 0.37 | 0.69 | 4.68 | 95.69 | 79.31 | 32.37 |
decrease in dipolar interaction between ‘d’ electron and nucleus. This may be due to increase in separation between d_{xy} electron and nucleus magnetic dipoles.

Both ‘P’ and the in-plane π-bonding wave function \( \beta^2 \) are lower for V10 glass. Least \( \beta^2 \) value implies that the d_{xy} orbital is less localised on vanadium atom in V10 glass than the other glasses of this series. This supports the least value of ‘P’ for V10 glass compared with others.

The isotropic parameters of g and A are calculated as

\[ g_{iso} = \frac{(2g \perp + g||)}{3}, \quad (5a) \]
\[ A_{iso} = \frac{(2A \perp + A||)}{3}. \quad (5b) \]

Fermi contact parameter \( k \) is given by expression (6)

\[ k = \frac{A_{iso}}{P - (ge - giso)}, \quad (6) \]

Not only d-electron, paired ‘s’ electron also contribute to the hyperfine interaction with the nucleus. Fermi contact term \( \kappa \) depends on the share of hyperfine splitting of s-orbitals. Large value of \( \kappa = 0.73 \) for V10 than the other glasses of the studied glass series indicates more interaction of ‘s’ electrons of vanadium with the nucleus and less contribution of 3d_{xy} unpaired electron to hyperfine interaction. Hence as \( \kappa \) decreases, \( P \) value increases [25].

Hyperfine coupling parameters \( A\parallel \) and \( A \perp \), hyperfine splitting parameters \( g\parallel, g\perp \) are related to molecular orbital coefficient \( \beta^2 \) as shown in equations (7) and (8) [31]. Here—P\kappa term is due to resultant contribution of the all the paired ‘s’ electrons of vanadium ion. \( A\parallel \) and \( A\perp \) correspond to the magnetic moment interaction between 3d_{xy} electron and the vanadium nucleus.

\[ A\parallel = -P\left[ \kappa + \frac{4}{7} \beta^2 + (ge - g\perp) + \frac{3}{7} (ge - g\parallel) \right] = -P\kappa + A\parallel. \quad (7) \]
\[ A \perp = -P\left[ \kappa - \frac{2}{7} \beta^2 + \frac{11}{14} (ge - g\perp) \right] = -P\kappa + A\perp. \quad (8) \]

Where \( ge (=-2.0023) \) is the unpaired electron g value.

Using \( P \) and \( \kappa \) in above equations the covalency ratio \( \beta^2 \) is calculated for the V = O bonds.

\( \beta^2 \) is the fraction of d_{xy} (ground state) orbital contribution in the corresponding nonbonding function. The value of \( \beta^2 = 1 \) when the orbital is purely nonbonding like pure VO(H2O)_{5+}. For studied glasses \( \beta^2 \approx 1 \) which indicates in-plane π-bonding is nearly ionic and the orbital is more localized on the vanadium atom only a little on ligand. Decrease in \( \beta^2 \) value from unity indicates admixture of ligand orbitals. The molecular orbital bonding coefficients \( \alpha^2 \) and \( \gamma^2 \) are evaluated correlating the EPR spectral data with optical bandgaps using the mathematical relations (9), (10) [31].

\[ \alpha^2 = \frac{\Delta g|| \Delta||}{4\lambda^2 \beta^2 \cdot ge}, \quad (9) \]
\[ \gamma^2 = \frac{\Delta g|| \Delta||}{\lambda^2 \cdot 32 \cdot ge}. \quad (10) \]

where \( \lambda \) is spin–orbit coupling constant of VO^{2+} (vandylic) ion [32].

\( \alpha^2 \) value depends on the nature of in-plane \( \sigma \)-bonding of vanadium 4s, 4p_x, 4p_y, 4p_z, 3d_{xz}, 3d_{yz} with ligand \( \sigma \)-orbitals, and \( \gamma^2 \) represents the out-of-plane π-bonding of 3d_{xy}, 3d_{yz} orbitals with vandyl oxygen [21].

(1−\( \alpha^2 \)) < 0.5 indicate that in-plane \( \sigma \)-bonding orbital is more localized on ligands than the vanadium atom.

(1 − \( \gamma^2 \)) values indicate that the out of plane π-bonding orbital is more localised on vanadium atom and partly on ligands. The Z_2 distortion in present glasses is mainly due to the out of plane π-bonds between 3d_{xy}, 3d_{yz} orbitals and the ligands, shown in figure 9(a). The ionic nature of glasses estimated from the physical parameters in table 2 also supports this (figure 9(b)). The in-plane \( \sigma \)-bonds and out of plane π-bonds between vanadium and it’s ligands are moderately covalent [31].

### 3.7 Vibrational spectra

Raman spectra and FTIR spectra were recorded in wavenumber range 400–4000 cm\(^{-1}\) and the noticed band centres of various structural groups are shown in figures 10(a) and (b) respectively. The assigned vibrational band positions are shown in table 5.

Band centres at 470 cm\(^{-1}\); 540 cm\(^{-1}\); 1080 cm\(^{-1}\) reveal the presence of vitreous silica and SiO\(_4\) with one NBO respectively. A band at 670 cm\(^{-1}\) is observed clearly in both FTIR and Raman spectra indicate Si – O – B vibration has asymmetric mode.
dependence of bonding parameter on tetragonal compression; (b) Dependence of $\frac{R_m}{V_m}$ on tetragonal compression of $x\text{Na}_2\text{O}-(30-x)\text{K}_2\text{O}-38\text{SiO}_2-30\text{B}_2\text{O}_3-2\text{V}_2\text{O}_5$ glass.

Figure 9. (a) dependence of bonding parameter on tetragonal compression; (b) Dependence of $\frac{R_m}{V_m}$ on tetragonal compression of $x\text{Na}_2\text{O}-(30-x)\text{K}_2\text{O}-38\text{SiO}_2-30\text{B}_2\text{O}_3-2\text{V}_2\text{O}_5$ glass.

Dependence of $R_m$ and $V_m$ on tetragonal compression of $x\text{Na}_2\text{O}-(30-x)\text{K}_2\text{O}-38\text{SiO}_2-30\text{B}_2\text{O}_3-2\text{V}_2\text{O}_5$ glass.

Figure 10. (a). Raman spectra; (b). FTIR spectra of $x\text{Na}_2\text{O}-(30-x)\text{K}_2\text{O}-38\text{SiO}_2-30\text{B}_2\text{O}_3-2\text{V}_2\text{O}_5$ glasses.

Table 5. Structural groups in $x\text{Na}_2\text{O}-(30-x)\text{K}_2\text{O}-38\text{SiO}_2-30\text{B}_2\text{O}_3-2\text{V}_2\text{O}_5$ glasses from Raman and FTIR spectra.

| S.No | Band centre position | Assigned band | References No. |
|------|----------------------|---------------|----------------|
| 1    | 450, 470             | O– Si–O vibrations of SiO$_4$ tetrahedra | [33–35]. |
| 2    | 540, 1080, 1105      | SiO$_4$ tetrahedra with 1 NBO | [35, 36] |
| 3    | 610, 1520            | Symmetric vibrations of 3–NBO in meta borate ring | [35, 37] |
| 4    | 670                  | Si–O–B asymmetric vibration modes | [34] |
| 5    | 720                  | Bent mode of B-O-B in 6 membered borate ring | [33, 34, 37] |
| 6    | 765                  | 6 membered borate ring consist of one or more BO$_3$ tetrahedra | [35, 37, 36] |
| 7    | 830, 860, 1265, 1440 | stretching vibrations of BO$_3$ units in pyro borate | [35, 37, 38, 36] |
| 8    | 905                  | V–O–V symmetric stretching modes | [39] |
| 9    | 1020                 | Vibrational modes of B-O in borate tetrahedra in diborate groups | [37] |
| 10   | 1380                 | presence of pyro borate, ortho borate groups containing (BO$_3$)$_2$ units | [37] |
Addition of alkali creates NBO by forming bonds with oxygen in Boroxol rings. So Boroxol rings break and various borate groups are formed. In the studied glasses too band at 806 cm\(^{-1}\) is not found, thus the Boroxol rings are absent. A strong band of 6- membered tri borate groups at 765 cm\(^{-1}\) is seen only in Raman not in FTIR spectra. It is probably due to symmetric vibration of the borate group. Meta borate, pyro borate groups are also observed respectively at band positions 610 cm\(^{-1}\); 830, 860 and 1250 cm\(^{-1}\) in Raman spectra only. So, it is interpreted as symmetric stretching of oxygen ions in borate groups [34, 35, 37, 38].

The V–O–V associated band at 910 cm\(^{-1}\) appears only in Raman spectra but not in FTIR, which implies that the triatomic molecule has symmetrical vibrational mode [36]. Bands at 450 and 470 cm\(^{-1}\) are observed in both the spectra revealing the presence of silica phase in the studied mixed alkali glasses. This supports the chemical stability of the studied glasses.

4. Conclusions

From the Physical, thermal and structural parameters of 2 mol% vanadyl doped \(38\text{SiO}_2-30\text{B}_2\text{O}_3-x\text{Na}_2\text{O}-(30-x)\text{K}_2\text{O}\) \((x = 5, 10, 15, 20, 25)\) glasses the following conclusions are drawn.

1. A long range disorder in structure was noticed in the XRD spectra for studied glasses.
2. The substitution of potassium oxide with sodium oxide in steps of 5 mol % from \(V_5\) to\(V_{25}\) in studied glasses shows decrease in their density, molar volume and inter ionic distance and increase in Transition metal concentration and Field strength.
3. Metallization criterion values reveal \(V_{10}\) glass had less covalent nature among the studied glasses.
4. It was clearly noticed from DTA curve supercooled temperature \(DT = T_{C1} - T_{g}\) is 110 °C for studied glasses. This indicates that the glasses had good ductile nature, so they could be used as sealants and to draw fibres.
5. Due to tetragonal compression of octahedron interstitial site of \(V^{4+}\), identical optical absorption bands with a slight shift was observed in all glasses.
6. Nonlinear changes are observed in optical bandgaps and band edge wavelength due to the mixed alkali effect.
7. Green emission at 350 nm excitation wavelength for these glasses may be because of the vacancies and defects present in glass.
8. Interpretations of EPR spectra confirm the \(V^{4+}\) ions occupy the centre of tetragonally compressed octahedron sites. Lower value in dipolar interaction constant \(P^d\) in comparison to the standard value of ionic bond in vanadyl complexes informs that the bond associated with d\(_{xy}\) electron and ligand has partly covalent nature.
9. Tetragonal compression measure \(\frac{\Delta x}{\Delta z}\) is more for \(V_{10}\) glass because e\(^-\) pair is nearer to vanadium than ligands for out of plane \(\pi\) - bonds than other studied glasses. So more tetragonal compression along \(z\) - axis for \(V_{10}\) glass than the other glasses. This conclusion was boosted from the metallization criterion value of studied glasses. \(V_{10}\) glass has more metallic nature than other glasses of this series.
10. \((1 - \alpha^2) < 0.5\) indicates indicates that the electron pair is localized more on ligands than vanadium atom for in-plane \(\sigma\) - bonding. \((1 - \gamma^2) > 0.5\) indicate that the out of plane \(\pi\) - bonding orbital is more localised on vanadium atom and partly on ligands. Both in-plane \(\sigma\) - bonding and out of plane \(\pi\) - bonding is moderately covalent and so these glasses are chemically stable materials.

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