Optical, EPR and FT-IR studies of VO²+ doped X Li₂O - (50-X) K₂O - 50 B₂O₃ (10 ≤ X ≤ 30) glasses

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ABSTRACT The effect of Li2O content in vanadyl doped X Li2O + (50-X) K2O + 50 B2O3 (10≤X≤30) (LKB) glasses has been studied with respect to their physical and structural properties. The physical parameters like density, refractive index, ionic concentration and electronic polarizability vary non-linearly with x mol% depending on the diffusivities of alkali ions. EPR and optical absorption spectra reveal that the resonance signals are characteristics of VO²+ ions in tetragonallycompressed octahedral site. Spin-Hamiltonian, crystal field, tetragonal field and bonding parameters are found to be in good agreement with the other reported glass systems. The optical band gap and Urbach energies exhibited the mixed alkali effect.

1. INTRODUCTION

Alkali borate glasses are of great technological interest especially lithium borates as solid electrolytes because of their fast ionic conduction. Borate glasses containing boron oxide have been widely used for optical lenses. Borate glasses are very interesting materials as shown by various diverse applications. Boron has the ability to change easily its coordination with oxygen between three and four. It can form variable structural units in borate glasses and crystals [1,2]. The borate glasses are very often investigated by different spectroscopic techniques because, which appears a large variety of structural units over a wide range of modifier concentration [3,4]. Some oxides, called glass former, have the ability to form glasses by themselves or by mixing with other network formers.

Borate glasses alone are not a stable compound even though it is well known as the glass former. It can easily crystallize after melting and it has hygroscopic properties which often limit their practical uses. So, in order to reduce the drawbacks and enhance the properties of glass, another oxide must be added to the system such as metal oxides or alkali oxides like Li_2O, Na_2O and K_2O. It can act as a network former and it has the ability to change the structural features of borate glass. Chemical composition of the glasses plays an important role in determining the properties. It has been observed quite generally in alkali modified network oxide glasses that the substitution of one alkali by another at a total fixed concentration of the alkalis gives rise to non-linear variation of properties exhibiting minima or maxima. The non-linear behavior of certain properties with respect to alkali content is known as the mixed alkali effect (MAE) [5].

In the recent years, the glasses doped with transition metal ions gained importance, because of their good spectroscopic properties and suitability for solid state lasers. Vanadium and copper ions are the simplest and well suited, since they are characterized by partially filled d shell which can exist in at least two valency states. Each of these valency states has a different electronic structure and coordination geometry. Electron paramagnetic resonance spectroscopy can used to determine the ratio of different

valance states in these glass systems [6, 7]. The vanadyl ions (VO²+) have been used as a spectroscopic probe for characterization of glasses [8-10]. VO²+ is the most stable and widely used EPR probe for probing the site symmetry of central metal ions and bonding nature with its ligands. The interesting behaviour of VO²+ ions in different crystalline matrices is due to different orientations of V-O ion. Most of the results reported for this ions can be classified into two groups, one in which the vanadyl ion freely rotates at normal temperatures and the second category in which it is preferentially oriented. V_2O_5 based glasses exhibit switching and semiconducting properties [11, 12] and used for making of stable switching devices [13, 14].

In the present work, the VO²+ doped LKB glasses were prepared by melt quenching technique. In order to identify the local structural changes caused by the mixed alkali ions variations as well as to obtain information about the local symmetry around the paramagnetic metallic ions the prepared samples were characterized by different physical and spectroscopic techniques.

2. Experimental Procedure
2.1 Preparation of glasses

Glass samples are prepared by the melt quench technique. 0.1 mol% of VO²+ doped mixed alkali borate glasses are prepared by using AR grade chemicals of Li_2CO_3, K_2CO_3, B_2O_3 and V_2O_5 as starting material with 99.9% of purity. The glass composition is taken in ratio as mentioned in the Table 1. Initially, the glass samples are prepared by taking suitable amounts of materials that are weighed and thoroughly mixed. These mixtures are sintered at 750 K and melted in an electric furnace in a silica crucible around 1150 K for nearly one hour. The melt is then quenched at room temperature in air to form a glass. The glass samples are transferred to another furnace and annealed at 700 K for 1 h to relive structural stress.

Table 1: Composition of VO²+ doped LKB glasses studied in the present work

Glass	Chemical Composition	Prepared temperature (K)

LKB1	$9.9\ Li_2O + 40\ K_2O +$ $50\ B_2O_3 + 0.1\ V_2O_5$	1173
LKB2	$19.9\ Li_2O + 30\ K_2O +$ $50\ B_2O_3 + 0.1\ V_2O_5$	1173
LKB3	$29.9\ Li_2O + 20\ K_2O +$ $50\ B_2O_3 + 0.1\ V_2O_5$	1173

2.2 Characterizations

The X-ray diffraction patterns of powder glass samples are recorded using Shimadzu 6100 with Cu Kα radiation of 1.5406 Å. The densities (D) of prepared glass samples are measured by using Archimedes method with Xylene as an immersion fluid using VIBRA HT/HTR instrument. The refractive indices of prepared samples are measured by ATAGO's Abbe refractometer. The optical absorption spectra of the samples are recorded using JASCO V-670 spectrophotometer in region 200-1400 nm. EPR spectra of the samples are measured by using JEOL-JES TE100 ESR spectrometer at X-band frequency with 100 KHz field modulation. FT-IR spectra of glass samples are recorded using Shimadzu IR Affinity-1S FT-IR spectrometer in the region 2000-400 cm^{-1} using KBr pellet method.

3. Results & Discussion

3.1. Powder X-ray diffraction studies

The X-ray diffraction patterns do not contain any sharp peaks which is a sign of amorphous material (not shown in figure). All the prepared glass samples confirm the glassy nature.

3.2. Physical properties

Physical parameters of the samples like dielectric constant, molar refractivity, molar volume, reflection loss and oxygen packing density are calculated from the measured values of densities and refractive indices of VO^{2+} doped LKB glasses.

Dielectric constant of the glass sample can be calculated by using refractive index [15].

$$\epsilon = n_d^2$$

By using refractive index, the reflection loss of the sample is given by Fresnel`s formula [16]

$$R = [(n_d - 1)/(n_d + 1)]^2$$

Molar refractivity of the glass sample can be calculated by using the formula [17]

$$R_M = [(n_d^2 - 1)/(n_d^2 + 2)]M/\rho$$

The molar volume of the samples can be obtained by using the formula

$$V_m = M/\rho$$

Here, M is the molecular weight and ρ is the density of the sample. The oxygen packing density of the glass sample can be calculated by using the following expression [18],

$$O = n/V_m$$

Where n is the number of oxygen atoms in the composition. The electronic polarizability of the glass samples can be evaluated by using the formula [19]

$$\alpha_e = 3(n_d^2 - 1)/4\pi N(n_d^2 + 2)$$

Here N is the number of vanadium ions per unit volume.

The inter ionic distance and polaron radius can be calculated by using the following formulae [20]

$$r_i = (1/N)^{1/3}$$

$$r_p = (1/2)(\pi/6N)^{1/3}$$

Density and refractive index are important parameters for calculating the other physical properties like dielectric constant, molar refractivity, molar volume, reflection loss and oxygen packing density. The error in density measurements and refractive indices are estimated to be ±0.004 g/cm^3 and ±0.0001. The evaluated density and refractive index value shows non-linearity with Li_2O content, but oppositely directed. The density value initially increases and reaches to maximum value at 20% thereafter decreases, whereas refractive index decreases and reaches the minimum at 20% and then increases with increase of Li_2O content due to MAE. All the physical parameters vary non-linearly with Li_2O content. For the borate glasses the dielectric polarization is strong with composition close to the diffusivity crossover where the ionic conductivity is weak [21]. The same phenomenon is observed for both the parameters like ionic concentration and electronic polarizability. Initially the ionic concentration is high at 10% and decreases with increasing of Li_2O concentration, where as electronic polarizability is minimum at 10%, with increasing of Li_2O it increases. So the ionic concentration and electronic polarizability are oppositely directed. The evaluated physical parameters are presented in   Table 2.

Table 2: Physical properties of VO^{2+} doped LKB glasses at room temperature

Physical parameter	LKB1	LKB2	LKB3
Average molecular Weight (g/mol)	75.53	69.08	62.65
Density (D)(g/cm^3) (± 0.004)	2.409	2.415	2.406
Refractive index (n_d) (± 0.0001)	1.6453	1.6427	1.6465
Optical dielectric constant (ϵ) (± 0.005)	2.706	2.696	2.709
Reflection loss (r)	0.0594	0.0590	0.0596
Molar refractivity (R_m) (cm^{-3}) (± 0.005)	11.377	10.462	9.566
MolarVolume (V_m) (cm^3/mol)	31.3462	28.6053	26.0392
Oxygen Packing density (O) (cm^3/mol)	63.80	69.917	76.807
Ionic Concentration (N) (10^{22} ions/cm^3) (±0.005)	0.191	0.207	0.228
Electronic polarizability (α_e) (10^{-24} ions/cm^3) (±0.005)	45.33	41.67	38.02
Inter ionic distance (r_i) (A) (± 0.005)	1.726	1.689	1.628
Polaron radius (r) (± 0.005)	0.697	0.679	0.657

3.3. Optical absorption studies

Fig. 1 shows the optical absorption spectra of VO^{2+} doped LKB glasses. The spectra consist of three bands, which are the characteristics of distorted octahedral with tetragonal site symmetry for all glass samples. In VO^{2+}, the single d-electron occupies t_{2g} orbital in octahedral crystal field and gives rise to $^2T_{2g}$ ground state. When excited, the electron occupies upper E_g orbital and gives ^2E_g term. Suppose VO^{2+} exist in an ideal octahedral symmetry, only one band arising from the transition $^2T_{2g} \rightarrow {}^2E_g$.
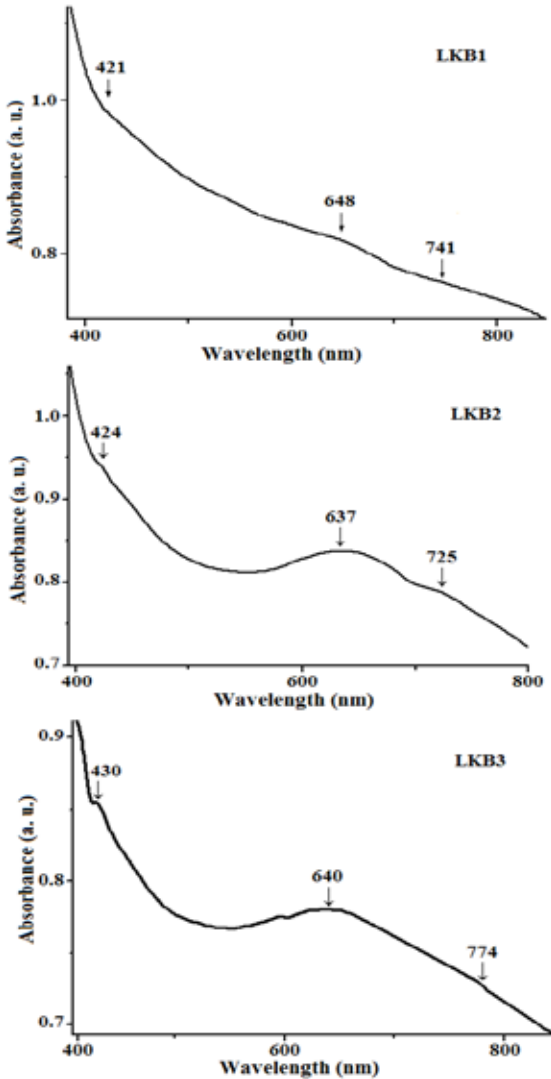
Fig. 1   Optical absorption spectra of VO²⁺ doped LKB glasses

Glass system	Transitions from $^2B_{2g}$	Wavelength (nm)	Wavenumber (cm⁻¹)	Dq (cm⁻¹)	Ds (cm⁻¹)	Dt (cm⁻¹)
LKB1	^2E_g	741	13495	1543	-3116	828
	$^2B_{1g}$	648	15432			
	$^2A_{1g}$	421	23753			
LKB2	^2E_g	725	13789	1569	-3096	900
	$^2B_{1g}$	637	15694			
	$^2A_{1g}$	424	23578			
LKB3	^2E_g	774	12916	1562	-2935	822
	$^2B_{1g}$	640	15620			
	$^2A_{1g}$	430	23249			

Table 3: Optical band positions, crystal field and tetragonal field parameters of VO²⁺ doped LKB glasses

There are two types of optical transitions, which can occur at the fundamental absorption edge of crystalline and non-crystalline semiconductors. They are direct and indirect transitions, in both the cases electromagnetic waves interact with the electron in valence band, which are raised across the fundamental gap to conduction band. In glasses, the glass forming anions influences the conduction band; the cations play an indirect but significant role. Urbach energy gives the width of the tails of localized states within the optical band gap. At the absorption edge, random internal electric fields will dominate the broadening of excitation levels due to the lack of long-range order or presence of defects [24-26]. The least ΔE, i.e., sharp absorption edge, suggests that defects are the minimum facilitating long-range order. The main feature of absorption edge of amorphous material is an exponential increase of absorption coefficient α(ν) with photon energy hν in accordance with the empirical relation [27].

$$\alpha(\nu) = \alpha_0 \exp(h\nu/\Delta E)$$

Here α_0 is constant, ν is the frequency of radiation and ΔE is Urbach energy. The absorption coefficient α(ν) can be obtained by using the following equation,

$$\alpha(\nu) = (1/d)\ln(I_0/I) = 2.303A/d$$

where A is absorbance at frequency ν and d is thickness of the sample. For an absorption by indirect transitions the equation of the form

$$E_{opt} = h\nu - (h\nu/B)^{1/2}$$

Using the above equations, by plotting $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ as a function of photon energy hν, one can find the optical energy band gaps (E_{opt}) for indirect and direct transitions respectively by extrapolating the linear region of the curve to hν-axis and are shown in Fig. 2 and Fig. 3 respectively. A graph is drawn between ln(α) and hν and from the graph slope is obtained, from the slope we can obtain the Urbach energy. Optical band gap energy initially increases with increase of Li_2O content and is maximum at x = 20 mol% thereafter it decreases.

However VO²⁺ never exist in an octahedral crystal symmetry, but lowers to the tetragonal one (C_{4v}). In C_{4v} symmetry, $^2T_{2g}$ splits in to $^2B_2$ and ^2E, whereas ^2E_g splits into $^2B_1$ and $^2A_1$. Due to this splitting three bands are arises due to the transition from ground state ($^2B_2$) to excited states (^2E, $^2B_1$, $^2A_1$). Generally the order of these levels are $^2B_2 < ^2E < ^2B_1 < ^2A_1$. The bands are assigned to these transitions $^2B_2 \rightarrow ^2E$, $^2B_2 \rightarrow ^2B_1$, $^2B_2 \rightarrow ^2A_1$. The crystal field (Dq) and tetragonal parameters (Ds and Dt) are obtained by using the equations.

The band assignments of transitions, crystal field parameter (Dq) and tetragonal field parameters (Ds and Dt) are presented in Table.3. These are in good agreement with other vanadyl doped borate glasses [22, 23].
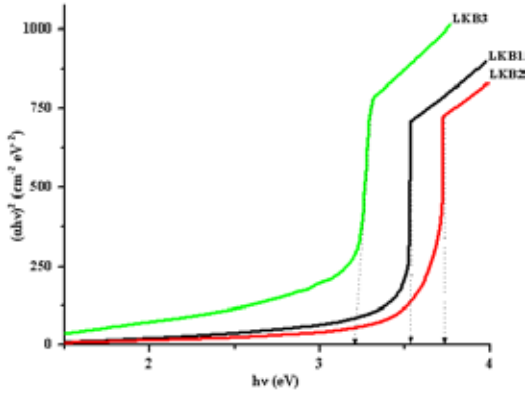
Fig. 2   Optical energy band gaps of VO²⁺ doped LKB glasses for direct transitions
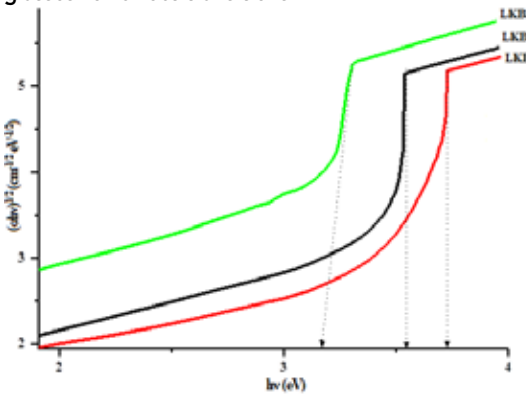

Fig. 3   Optical energy band gaps of VO²⁺ doped LKB glasses for indirect transitions

This non-liner variation of optical band gap energy shows the evidence of MAE in optical properties of LKB glasses, the same phenomenon is observed in Urbach energy as shown in Fig. 4.
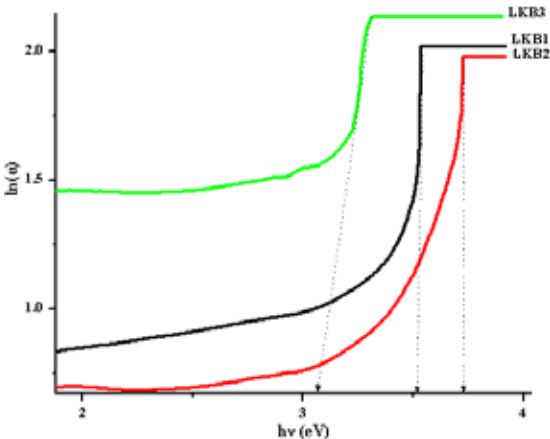

Fig. 4 Urbach energy curves of VO²⁺ doped LKB glasses

It is also interesting to observe that the Urbach energy decreases with x and reach a minimum around x = 20 mol% and thereafter increases, which shows MAE. The calculated values of optical band gap energy and Urbach energies are presented in the Table 4.

Table 4: Direct, Indirect band gap & Urbach energies of Mn²⁺ doped LKB glasses

Glass system	Optical band gap energy E_{opt} (eV)			Urbach energy ΔE (eV)
	Theoretical	Experimental		
		Direct	Indirect	
LKB1	3.579	3.535	3.532	0.0177
LKB2	3.685	3.696	3.693	0.0175
LKB3	3.225	3.212	3.210	0.1015

3.4. EPR studies

EPR spectra of VO²⁺ doped LKB glasses exhibit poorly resolved hyperfine signal as shown in Fig. 5. Generally, the coordination of vanadium is octahedral with tetragonal distortions [28]. The low resolution and unresolved signals of hyperfine couplings confirms the presence of V⁴⁺ species in an axially symmetrical environment. In the present investigation, the spin-Hamiltonian parameters of VO²⁺ doped LKB glasses were evaluated which are in good agreement with literature. An octahedral site symmetry with a tetragonal compression would give values of $g_\parallel < g_\perp < g_e$ and $A_\parallel > A_\perp$ [29]. The present values of the spin-Hamiltonian parameters agree with the above condition. From this observation, it is suggested that the paramagnetic V⁴⁺ ions in a frame work exist as the vanadyl ions, VO²⁺ in an octahedral environment of oxygen with tetragonal distortion (C_{4v}).
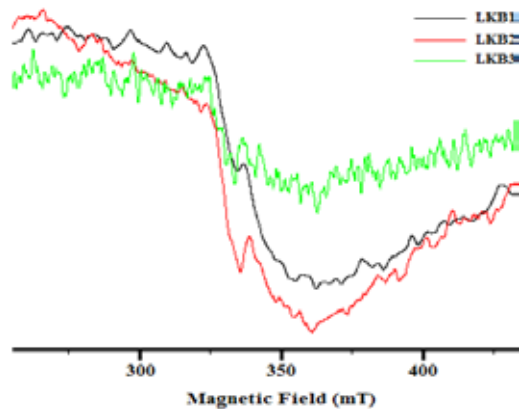

Fig. 5 EPR spectra of VO²⁺ doped LKB glasses

By correlating EPR and optical parameters, the molecular bonding coefficients β_1^2, β_2^2 and γ^2, the Fermi contact term κ and the dipolar hyperfine coupling constant P can be determined from the following expressions [30, 31]:

$$g_\parallel = g_e \left[1 - (4\lambda\beta_1^2\beta_2^2)/\Delta_\parallel \right]$$

$$g\perp = g_e \left[1 - (\lambda\gamma^2\beta_2^2)/\Delta\perp \right]$$

$$A_\parallel = -P \left[\kappa + (4/7)\ \beta_2^2 + (g_e - g_\parallel) + 3/7(g_e - g\perp) \right]$$

$$A\perp = P \left[2/7 - \kappa + 11/4\ (g\perp - g_e) \right]$$

where $g_\parallel$ and $g_\perp$ are related to the bonding parameters and ge (2.0023) is the free electron g value. $_\lambda$ is the free ion value of spin orbit coupling constant for VO²⁺ ion and is equal to 170 cm⁻¹. $\Delta_\parallel$ and $\Delta_\perp$ are energy separations from the ground state $^2B_{2g}$ to the two nearest higher states ^2E_g and $^2B_{1g}$ respectively. β_1^2, β_2^2 and γ^2 are the molecular bonding coefficients of the d^1 electron. β_1^2 and γ^2 are measures of the degrees of σ and π bonding with equatorial ligands respectively. β_2^2 is the covalency ratio of V=O bonds. The degree of distortion can be estimated from Fermi contact terms κ and the P parameter. P is related to the radial distribution of the wave function of the ions and is defined as $P = g_e g_N \beta_e \beta_N \langle r^{-3} \rangle$. The dipolar coupling con-

stant (P) is evaluated by ignoring the second order effects and taking negative values for $A_\parallel$ and $A_\perp$ [32].

$$P = 7(A_\parallel - A_\perp)/(6 + (3\lambda/2\Delta_\parallel))$$

The isotropic and anisotropic (g and A) parameters are determined using the formulae,

$$g_{iso} = (2g_\parallel + g_\perp)/3$$

$$A_{iso} = (2A_\parallel + A_\perp)/3$$

Using the above expressions one can gets

$$\kappa = - (A_{iso}/P) - (g_e - g_{iso})$$

and the Fermi contact parameter is evaluated. Using P and κ values, the bonding parameters β_1^2, β_2^2 and γ^2 are evaluated. The evaluated spin-Hamiltonian parameter are presented in Table 5. The deviation of β_2^2 from unity usually represents the degree of admixture of the ligand orbitals and increase in the degree of covalency. In the present study, β_2^2 is clearly indicates that the bonding is nearly ionic and represents poor π bonding of the ligands. However, κ value is lower than β_2^2 and nearly equal to unity. The deviation of κ from unity indicates the admixture of the 4s orbital into the d_{xy} orbital. It may be due to a low symmetry ligand field.

If $\beta_1^2 = 1$, the bond would be completely ionic. If $\beta_1^2 = 0.5$, the bond would be completely covalent. The parameters $(1 - \beta_1^2)$ and $(1 - \gamma^2)$ are the measures of the covalency. The first term gives an indication of the influence of σ bonding between the vanadium atom and equatorial ligands, while the second indicates the influence of π bonding between the vanadium ion and the vanadyl oxygen. The bonding coefficients β_1^2, β_2^2 and γ^2 characterize in plane σ bonding, in plane π bonding and out of plane π bonding respectively. In the present investigation, β_1^2, γ^2 are lower than β_2^2, which indicating that the in plane σ bonding, out of plane π bonding are more covalent than the in plane π bonding.

Table 5: The anisotropic g factors and the hyperfine structure constants (in 10^{-4} cm^{-1}) of VO^{2+} doped LKB glasses

Glass	$g_\parallel$	$g_\perp$	$A_\parallel$	$A_\perp$	κ	P
LKB1	1.9310	1.9798	172.08	54.50	0.64	137.01
LKB2	1.9312	1.9839	171.61	54.38	0.64	137.09
LKB3	1.9331	1.9810	173.65	56.53	0.66	137.55

3.5. FT-IR studies

FT-IR spectra can be used for the characterization of local order and the type of building structural units in oxide glasses [33]. IR spectra of the glasses exhibited absorption peaks which are sharp, medium, weak and broad. The vibrational mode of borate network seems to be mainly active in three IR regions which are similar to those reported by Kamitsos et al. [34]. The first groups of bands which occur at 1200-1600 cm^{-1} are due to the asymmetric stretching relaxations of B-O bond of trigonal BO$_3$ units. The second group lying between 800 and 1200 cm^{-1} is due to B-O bond stretching of the tetragonal BO$_4$ units and the third group is observed around 700 cm^{-1} and it is due to the bending of B-O-B linkages in the borate network. Li cation bands are observed in 417-519 cm^{-1} [35]. IR spectra of VO^{2+} doped LKB glasses are shown in Fig. 6. Bands in the region 415-519 cm^{-1} are assigned to specific vibrations of Li cations. The absorption band at 719-725 cm^{-1} is

due to B-O-B bending vibrations. Bands in 832-1169 cm^{-1} region are assigned to B-O symmetric stretching vibrations of BO$_4$ units. The absorption bands around 1215-1435 cm^{-1} are due to symmetric stretching vibrations of B-O bonds in trigonal BO$_3$ units. The absorption bands around 1661-1749 cm^{-1} are assigned to H-O-H bending vibrations. The assignments of bands are represented in the Table 6.

Table 6: Assignments of FT-IR bands in VO^{2+} doped LKB glasses

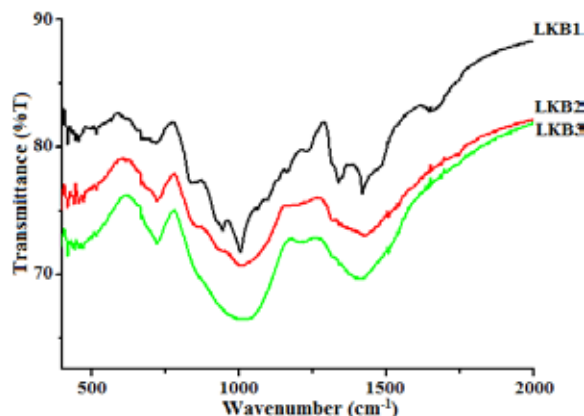| LKB1	LKB2	LKB3	Assignments
415,458, 519	418,444, 476,516	418,458, 470	Specific vibrations of Li cations
719	725	722	B-O-B bending vibrations
832,945, 1003,1169	850,931, 1009	1012	B-O symmetric vibrations of BO$_4$
1232,1334, 1421	1314,1435	1215,1337, 1409	B-O stretching vibrations of BO$_3$
1661	1749	1705	H-O-H bending vibrations

Fig. 6 IR spectra of VO^{2+}doped LKB glasses

4. Conclusion

From the physical and spectroscopic properties of VO^{2+} doped LKB glasses, the following conclusions are drawn:

(i) X-ray diffraction studies confirm the amorphous nature of the glasses.

(ii) Physical parameters like density, refractive index, molar refractivity, ionic concentration, electronic polarizability, inter-ionic distances and ionic radii varies non-linearly with respect to the changes in alkali concentration. This is due to the phenomena of MAE.

(iii) Optical absorption spectra exhibit characteristic bands of VO^{2+} ions in LKB glasses. EPR spectra exhibit poorly resolved hyperfine patterns of VO^{2+} doped LKB glasses.

(iv) Optical absorption and EPR studies confirm the tetragonally compressed distorted octahedral site symmetry for VO^{2+} ions with partial covalency of LKB glasses.

(v) From optical absorption edges, optical band gap energies and Urbach energies are evaluated. A non-linear behavior is observed and found to be in good agreement with theoretical values.

(vi) The non-linear behavior in g and A values was observed by changing the concentrations of alkali con-

tents which is the appearance of mixed alkali effect in the present glasses.

(vii) The FT-IR spectral analysis confirms the presence of BO_3 and BO_4 local structures in all the glass systems.

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