

Mixed Alkali Effect in Mn^{2+} Doped $\text{XLi}_2\text{O} + (50-X)\text{K}_2\text{O} + 50\text{B}_2\text{O}_3$ ($10 \leq X \leq 30$) Glasses

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Abstract: Divalent Mn^{2+} containing $\text{xLi}_2\text{O} + (50-x)\text{K}_2\text{O} + 50\text{B}_2\text{O}_3$ ($10 \leq x \leq 30$) (LKB glasses) mol% glasses are prepared by using melt quench technique. Various physical parameters are evaluated from measured values of density and refractive index for observation of mixed alkali effect. Structural changes of Mn^{2+} doped LKB glasses are investigated by optical absorption, electron paramagnetic resonance and FT-IR spectroscopic studies. The EPR spectra of Mn^{2+} doped LKB glasses exhibited a characteristic hyperfine sextet around $g = 2.02$. The optical band gap and Urbach energies are calculated which confirmed the mixed alkali effect. FT-IR measurements of all glasses revealed that the network structure of glass system is mainly based on BO_3 and BO_4 units placed in different structural groups.

Keywords: Alkali borate glasses, Mixed alkali effect, Melt quench technique, Electron paramagnetic resonance

1. Introduction

Mixed alkali glasses are unique from the point of view of certain properties, as their change is much more than normally anticipated. The structure of mixed alkali glasses appears to be simple when one alkali oxide is substituted for another. Mixed alkali effect is observed in silicate, borate and phosphate glasses [1-3]. Keeping in view of underlying physics and applications of MAE the certain glass systems have been selected for density and optical studies. Electron spin resonance (ESR) spectroscopy is an experimental technique, proficient in determining the coordination and environment of paramagnetic ions in glasses. Optical absorption spectrum of transition metal ions in glass is influenced by host glass structure when the transition metal ions are incorporated into it. In oxide glasses, the transition metal ions mostly form coordination complexes with doubly charged oxygen as the ligands. By correlating the ESR and optical spectral data, one can obtain information regarding the bond parameters which determines the metal ligand bond in the glass.

The challenging research work has been done on optical properties of transition metal ions showing non-linear behaviour. Owing to their prospective applications in solid state devices, electro-optic modulators, electric and electro-optic devices [4]. In the present investigation, we tried to dope Mn^{2+} ions into borate glass using B_2O_3 as a glass former with variable alkali content and studied their EPR and optical spectra. Borate glasses are very fascinating amorphous materials due to their explicit physical and structural properties. The borate glasses are mainly exhibiting two groups of bands namely trigonal BO_3 and tetragonal BO_4 units [5]. Alkali borate glasses are particularly interesting network frames as they exhibit a verity of structural changes due to variable alkali content. Lithium containing alkali borate glasses are creating abundant technological interest in the field of solid electrolytes owing to their fast ionic conducting nature. Hence, the borate glasses are remarkable as inorganic hosts for transition metal ions [6].

Over the last few decades, pronounced significance has been given to the transition metal ions doped glass. As the possess intensive spectroscopic behaviour in their 3d electrons [7, 8]. Transition metal ions are known to influence the optical, electrical and magnetic properties of glasses due to their highly sensitive response and their ability to possess more than one valence state. Further, these ions can be used as better candidates to probe the glass structure due to their broad radial distribution of outer d orbital electrons and their sensitive response to the surrounding cations [9]. Among these transition metal ions manganese has been frequently used as paramagnetic probe for exploring the structure and spectroscopic properties of vitreous systems. Generally the EPR spectrum of these glasses exhibit a six-line hyperfine structure at $g = 2.01$ only due to the presence of Mn^{2+} ions (d^5 configuration). Non-linear behaviour in physical properties of lithium potassium borate glasses doped with MnO_2 and Fe_2O_3 are observed by Padmaja et al. [10].

2. Experimental Procedure

2.1 Preparation Technique

Series of manganese doped mixed alkali borate glasses are prepared by using analar grade chemicals of Li_2CO_3 , K_2CO_3 , B_2O_3 and MnO with 99.9% of purity. These mixtures are sintered at 750 K and melted in an electric furnace in a silica crucible around 1173 K for 1 hour. The melt is then quenched at room temperature in air to form a glass. The glasses are further annealed at 700 K for 1 h to remove the structural strains. The glass composition is here after named as LKB glass series. The molar glass composition is taken as per the Table 1.

Table 1: Comparison of Mn²⁺ doped LKB glasses studied in the present work

Glasses	Chemical composition	Prepared temperature (K)
LKB1	9.9Li ₂ O+40K ₂ O+50B ₂ O ₃ +0.1MnO	1173
LKB2	19.9Li ₂ O+30K ₂ O+50B ₂ O ₃ +0.1MnO	1173
LKB3	29.9Li ₂ O+20K ₂ O+50B ₂ O ₃ +0.1MnO	1173

2.2 Characterizations

The density (D) of all the glasses is determined by Archimedes method with Xylene as an immersion fluid using VIBRA HT/HTR instrument. Refractive indices of the prepared glasses are measured using ATAGO's Abbe refractometer. The optical absorption spectra of the glasses are taken from JASCO V670 spectrophotometer in the region of 200-1400 nm. EPR spectra of the prepared samples are recorded at room temperature using JEOL JES TE100 ESR spectrometer at X-band frequency 100 KHz field modulation. The FT-IR spectra are recorded by using KBr pellets on Shimadzu IR Affinity-1S in the range of 2000-400 cm⁻¹.

3. Results and Discussion

3.1 Physical Properties

Various physical parameters like dielectric constant, reflection loss, molar refractivity, molar volume and oxygen packing density are evaluated from the measured values of densities and refractive indices of Mn²⁺ doped LKB glasses. The dielectric constant of glasses can be calculated from the refractive index by using the equation below [11].

$$\epsilon = n_d^2 \text{ ----- (1)}$$

By using refractive index the reflection loss of the glass is given by Fresnel's formula [12]

$$R = [(n_d - 1)/(n_d + 1)]^2 \text{ ----- (2)}$$

The molar refractivity R_M for each glass can be calculated using the formula [13]

$$R_M = [(n_d^2 - 1)/(n_d^2 + 2)]M/D \text{ ----- (3)}$$

Molar volume of the glasses can be calculated from following expression:

$$V_m = M/D \text{ ----- (4)}$$

where M is the molecular weight and D is the density of the sample. The oxygen packing density of the glasses can be evaluated using the following relation [14]

$$O = n/V_m \text{ ----- (5)}$$

where n is the number of oxygen atoms in the composition. The electronic polarizability (α_e) of the glass samples can be evaluated by using the following formula [15]

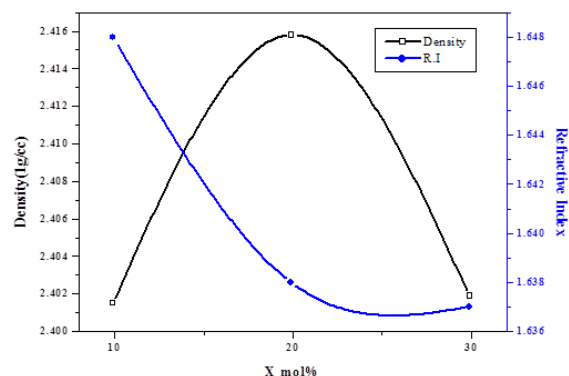
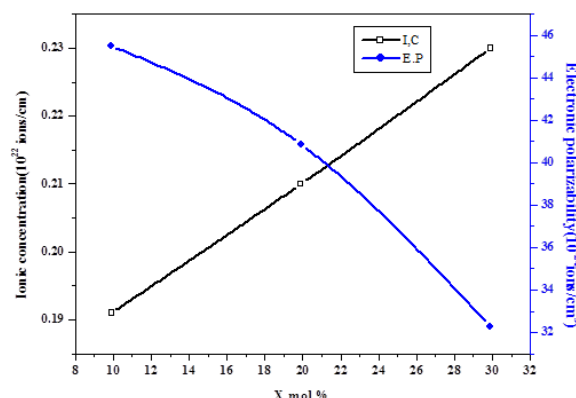
$$\alpha_e = 3(n_d^2 - 1)/4\pi N(n_d^2 + 2) \text{ ----- (6)}$$

where N is the number of manganese ions per unit volume. The inter-ionic distance and polaron radius can be calculated by using the following formulae [16]

$$r_i = (1/N)^{1/3} \text{ ----- (7)}$$

$$r_p = (1/2)(\pi/6N)^{1/3} \text{ ----- (8)}$$

Fig.1 and Fig. 2 show the effect of Li₂O content on density versus refractive index and ionic concentration versus electronic polarizability of Mn²⁺ doped LKB glasses respectively.

**Figure 1:** Composition dependence of density and refractive index of Mn²⁺ doped LKB glasses**Figure 2:** Composition dependence of ionic concentration and electronic polarizability of Mn²⁺ doped LKB glasses

The curves corresponding to ionic concentration and electronic polarizability exhibiting a non-linear trend with respect to the change of alkali content. It is observed that the electronic polarizability of the system is low at x = 30 mol% whereas the ionic concentration is high, which is undeviating observation of MAE in the present glasses. Density increases and refractive index decreases with increase of Li₂O content. It is also observed that the inter-ionic distance and polaron radius decreases with increase of Li₂O content. This is due to the modifying ions tending to occupy interstitial sites within the glass network. Therefore, a greater mass exists in just slightly increased volume of the glass. However, the increase is not linear, probably due to the formation of various boroxyl groups which may change the volume of the glass. Non-linear behaviour of physical properties displayed is due to the change in mol% of Li₂O content. This confirms the MAE in LKB glasses. In Table 2 the physical properties of Mn²⁺ doped LKB glasses are presented.

Table 2: Physical properties of Mn²⁺ doped LKB glasses at room temperature

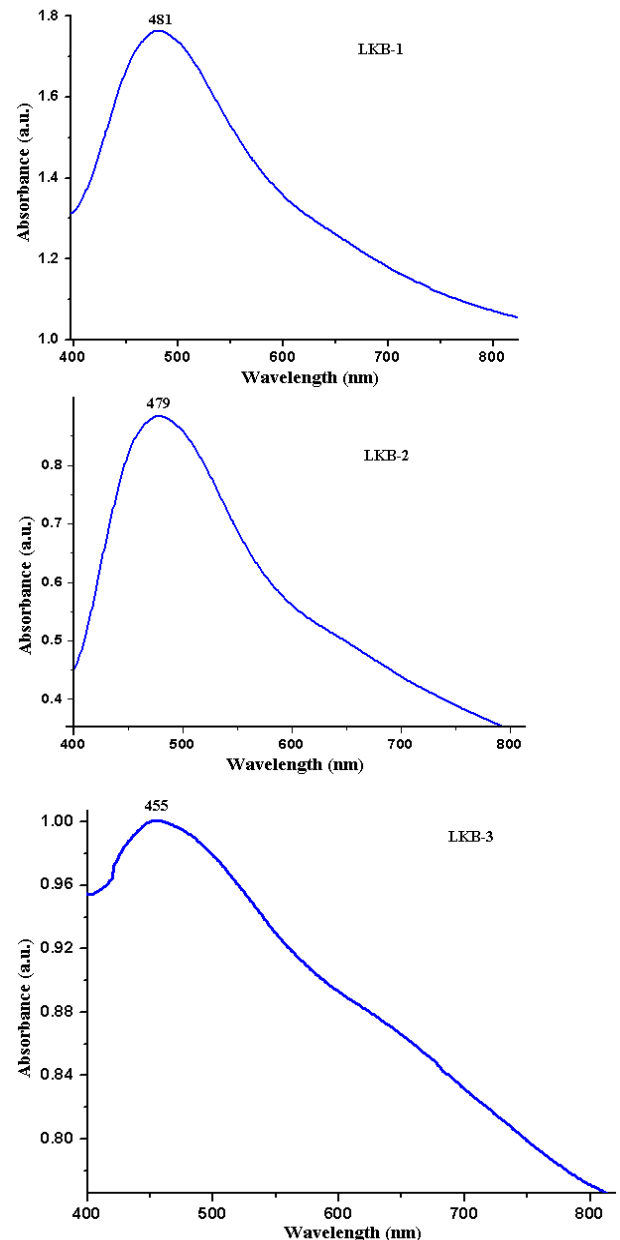
Physical Parameter	LKB1	LKB2	LKB3
Average molecular weight (g/mol)	75.51	69.08	62.65
Density (D)(g/cm ³) (± 0.004)	2.4015	2.4158	2.4019
Refractive index (n _d) (± 0.0001)	1.6485	1.6383	1.6374
Optical dielectric constant (ε) (± 0.005)	2.715	2.683	2.679
Reflection loss (r)	0.0598	0.0584	0.0583
Molar refractivity (R _m) (cm ³) (± 0.005)	11.446	10.281	9.368
Molar Volume (V _m) (cm ³ /mol)	31.4461	28.5975	26.0854
Oxygen Packing density (O) (cm ³ /mol)	63.6009	69.9360	76.6711
Manganese ion concentration (N) (10 ²² ions/cm ³) (± 0.005)	0.191	0.210	0.230
Electronic polarizability (α _e) (10 ⁻²⁴ ions/cm ³) (± 0.005)	45.50	40.87	32.27
Inter ionic distance (r _i) (Å) (± 0.005)	1.726	1.673	1.624
Polaron radius (r _p) (Å) (± 0.005)	0.697	0.675	0.655

3.2 Optical Absorption Studies

Electronic configuration of Mn²⁺ (d⁵) gives rise to free ion terms ⁶S, ⁴P, ⁴F, ⁴G in addition to a number of doublet states of which ⁶S occupies the ground state. ⁶S and ⁴P terms transform as ⁶A_{1g} and ⁴T_{1g} respectively, in crystal fields. ⁴D and ⁴F splits into ⁴E_g + ⁴T_{2g} and ⁴A_{1g} + ⁴E_g + ⁴T_{1g} + ⁴T_{2g} respectively. The optical absorption spectra of Mn²⁺ doped LKB glasses exhibit band at 481, 479 and 455 nm for LKB1, LKB2 and LKB3 respectively, which reveal the characteristic absorption of distorted octahedral site symmetry and shown in Fig. 3 for LKB1, LKB2 and LKB3 glasses. The band position is assigned to the transition ⁶A_{1g}(S) → ⁴T_{1g}(G). The observed shifting in band position is significant with increase of Li₂O content, which signifies MAE.

3.2.1 Optical Bandgap and Urbach Energies

The absorption edge in UV region is used to investigate the optical transitions, electronic band structure in crystalline and non-crystalline materials. Two types of optical transitions occur at the fundamental absorption edge of crystalline and non-crystalline materials, namely direct and indirect transitions. In these cases, electromagnetic waves interact with the electrons in the valence band, which jumps up to the conduction band. In case of glasses, conduction band is influenced by the anions, but the cations play an indirect major role.

**Figure 3:** Optical absorption spectra of Mn²⁺ doped LKB glasses

The absorption co-efficient α (ν) is a function of photon energy for direct and indirect transitions [17] can be written as

For direct transitions,

$$\alpha(\nu) = A(h\nu - E_{\text{opt}})^n / h\nu \text{ ----- (9)}$$

Here $n = 1/2$ for allowed transition, A is constant and E_{opt} is direct optical bandgap.

For indirect transitions,

$$\alpha(\nu) = A(h\nu - E_{\text{opt}})^n / h\nu \text{ ----- (10)}$$

Here $n = 2$ for allowed transition, A is constant and E_{opt} is the indirect optical bandgap. The plots for $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ as a function of photon energy $h\nu$ with respect to the above equations. The direct and indirect bandgaps are shown in Fig. 4 and Fig. 5. The respective values of E_{opt} for direct and

indirect transitions are obtained by extrapolating to $(\alpha h\nu)^2 = 0$ for direct and $(\alpha h\nu)^{1/2} = 0$ for indirect transitions. The optical bandgap energy is obtained by extrapolating the linear region of the curve to $h\nu$ -axis.

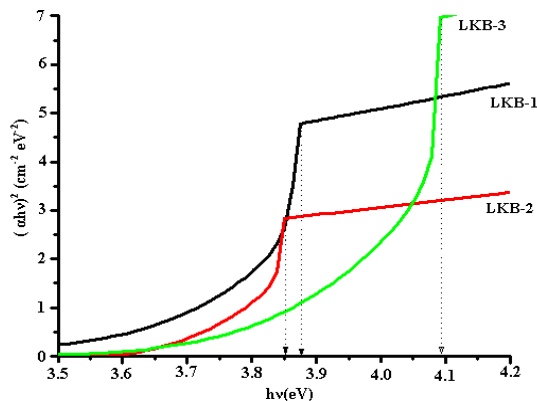


Figure 4: Direct bandgap energy diagram of Mn^{2+} doped LKB glasses

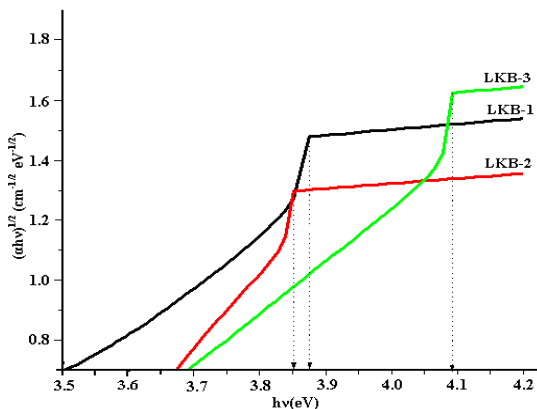


Figure 5: Indirect bandgap energy diagram of Mn^{2+} doped glasses

From these plots the optical band gap energies are given in the Table 3. The theoretical value can be obtained by using the following formula

$$E_{opt} = hc/\lambda \text{ ----- (11)}$$

The optical band gap energy shows the non-linear behaviour of these LKB glasses, which is maximum at 10 mol% thereafter it decreases at 20 mol% and then increases. The main feature of absorption edge of amorphous material is an exponential increase of absorption coefficient $\alpha(\nu)$ with photon energy $h\nu$ in accordance with the empirical relation [18]

$$\alpha(\nu) = \alpha_0 \exp(h\nu/\Delta E) \text{ ----- (12)}$$

where α_0 is constant ν is the frequency of radiation and ΔE is the Urbach energy which indicates the width of band tails of localized states and depends on temperature, static disorder, induced disorder and average photon energies. Hence, Urbach energy is used to measure disorder in amorphous and crystalline materials [19, 20]. The static atomic structural disorder dominates and can be due to presence of defects like dangling bonds or non-bridging oxygens in glasses [21].

Urbach energies (ΔE) are calculated by taking the reciprocals of slopes of linear proportion in the lower photon energy regions of these curves are shown in Fig. 6 and the values are listed in the Table 3. Urbach energy is initially maximum and decreases with increase of Li_2O content which shows MAE. It also shows the structural disorder of the system. Smaller is the value of Urbach energy, greater is the structural stability of glasses.

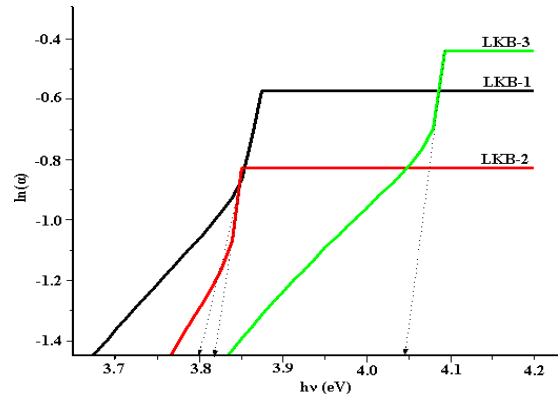


Figure 6: Urbach energy plots of Mn^{2+} doped LKB glasses

Table 3: Direct, Indirect band gap & Urbach energies of Mn^{2+} doped LKB glasses

S. No	Glasses	Optical band gap energy E _{opt} (eV)			Urbach energy ΔE (eV)
		Theoretical	Experimental		
			Direct	Indirect	
1	LKB1	3.881	3.876	3.875	0.081
2	LKB2	3.857	3.852	3.851	0.051
3	LKB3	4.099	4.093	4.092	0.049

3.3 EPR Studies

The EPR spectra of Mn^{2+} doped LKB glasses are shown in Fig. 7.

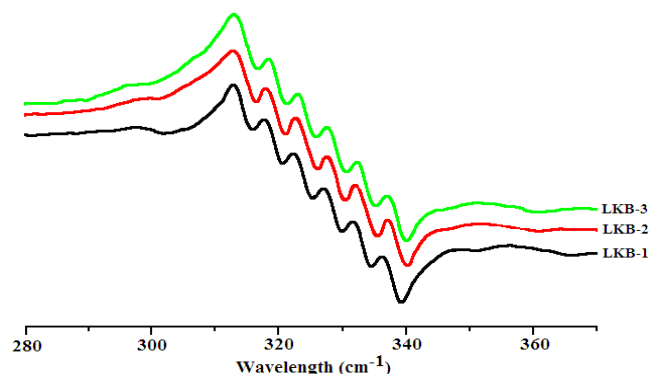


Figure 7: EPR spectra of Mn^{2+} doped glasses at room temperature

In general, EPR spectra of Mn^{2+} are analyzed by using spin-Hamiltonian of the form,

$$H = g\beta BS + SAI + SDS \text{ ----- (13)}$$

where g is isotropic factor, β is Bohr magneton, B is external magnetic field, S is vector operator of the electron spin momentum and A is hyperfine interaction parameter, I is vector operator of nuclear spin momentum and D is zero field

splitting parameter. Investigations of the EPR spectra of Mn^{2+} in variety of glasses are characterized by an intense resonance signal at $g = 2.0$ with a hyperfine structure and absorption band around $g = 4.3$ and a distinct shoulder at $g = 3.3$ [22]. Each fine structure transition splits into six hyperfine components due to interaction of electron spin with ^{55}Mn nucleus, having spin $I = 5/2$. Spin-Hamiltonian, bonding and zero field splitting parameters are given in the Table 4. The composition dependence of g and A parameters of Mn^{2+} doped LKB glasses is shown in Fig. 8.

Table 4: Spin-Hamiltonian and zero field splitting parameters of Mn^{2+} doped LKB glasses

Glasses	g value	A (10^{-4} cm^{-1})	$\Delta g = g_e - g$	$D(\text{mT})$
LKB1	2.0193	83.71	-0.017	75
LKB2	2.0200	84.98	-0.0177	75
LKB3	2.0241	83.26	-0.0218	75

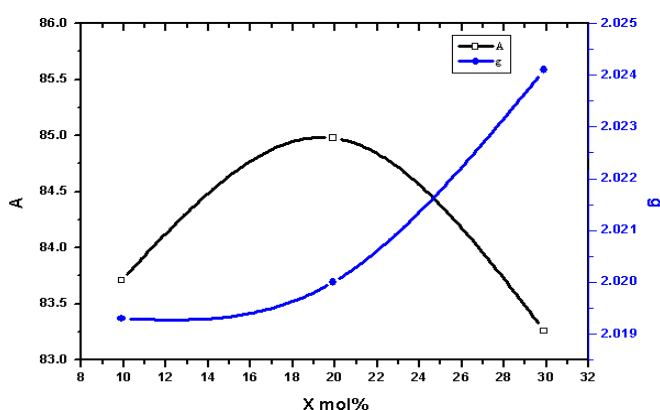


Figure 8: Composition dependence of g and A parameters of Mn^{2+} doped LKB glasses

It is observed that the value of g and A varies nonlinearly with Li_2O content. The value of g for Mn^{2+} transition ($-1/2$ to $+1/2$) varies nonlinearly along with D , reaches to maximum at $x = 20$ mol% where A is minimum. The abrupt change is observed in spin-Hamiltonian and bonding parameters diffusivity crossover point i.e. at $x = 20$ mol%. The anomaly behaviour at this point may be caused due to strong fields of manganese ions, where its g value is large. According to Van Wieringen, there is a regular variation of hyperfine coupling constant with covalence [23]. The g value for the hyperfine splitting indicates the bonding nature. If g value shows a negative shift with respect to the free electron value (2.0023), then the bonding is ionic and if the shift is positive, then the bonding is more covalent in nature. The negative value of Δg confirms the covalent bonding of LKB glasses and it is observed non-linearity with the increase of Li_2O content.

3.4 FT-IR Studies

FT-IR spectroscopy can be used to determine various structural units present in the glass network. It is well-known to provide insight into the interaction between alkali metal ions and borate glass network. Absorption of these alkali borate glasses is very high in the region of interest of wave numbers $< 2000 \text{ cm}^{-1}$. The spectrum can be divided into three regions such as $600\text{--}800 \text{ cm}^{-1}$ is due to B-O-B bending vibrations of various borate arrangements, the region $800\text{--}1200 \text{ cm}^{-1}$ is attributed to B-O symmetric vibrations of

tetrahedral BO_4 units and $1200\text{--}1600 \text{ cm}^{-1}$ region related to B-O stretching vibrations of BO_3 units [24-26]. The modifier oxides like Li_2O and K_2O may enter the glass network by transforming sp^2 planar BO_3 units into most stable sp^3 tetrahedral BO_4 units and may also create non-bridging oxygens. The results reveal that both BO_3 and BO_4 units co-exist in these glasses [27-29]. The FT-IR spectra of Mn^{2+} doped $x \text{ Li}_2\text{O} + (50-x) \text{ K}_2\text{O} + 50 \text{ B}_2\text{O}_3$ ($10 \leq x \leq 30$) LKB glasses are shown in Fig. 9.

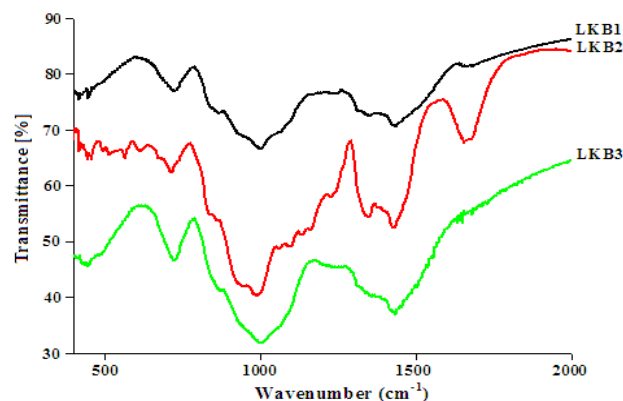


Figure 9: FT-IR spectra of Mn^{2+} doped LKB glasses

Boron has smallest mass as compared to other network forming elements and thus main vibrational modes associated with the glass network appear well above 500 cm^{-1} . The absorption bands in the region $444\text{--}568 \text{ cm}^{-1}$ are due to specific vibrations of Li cations [30]. The bands in the region $613\text{--}724 \text{ cm}^{-1}$ are due to B-O-B bending vibrations. The absorption bands in the region $837\text{--}1162 \text{ cm}^{-1}$ are assigned to B-O symmetric vibrations of BO_4 units. The absorption bands observed around 1230 and 1434 cm^{-1} are assigned to B-O stretching vibrations of BO_3 units. The absorption bands around 1669 cm^{-1} are assigned to H-O-H bending vibrations. The obtained absorption bands and their assignments are summarized in Table 5.

Table 5: Assignments of FT-IR bands in Mn^{2+} doped LKB glasses

Band position (cm^{-1})			Assignments
LKB1	LKB2	LKB3	
449	460,494,5 17,568	444	Specific vibration of Li cations
724	613,715	724	B-O-B bending vibrations
865,930, 1004, 1069	837,942,9 90,1060,1 100,1134, 1162	868, 1001	B-O symmetric vibrations of BO_4
1315,1352, 1429	1230,134 6,1431	1434	B-O stretching vibrations of BO_3
1666	1669	----	H-O-H bending vibrations

4. Conclusion

The physical and spectral properties of $0.1 \text{ mol } \%$ of Mn^{2+} doped $x \text{ Li}_2\text{O} + (50-x) \text{ K}_2\text{O} + 50 \text{ B}_2\text{O}_3$ ($10 \leq x \leq 30$) glasses are studied and the following conclusions are made:

The physical properties namely density, refractive index, optical dielectric constant, refraction loss, molar refractivity, manganese ion concentration, electronic polarizability, inter-ionic distance and polaron radii are observed to vary non-linearly with x mol% of alkali content which confirms the presence of the MAE. From optical absorption edges the optical bandgap and Urbach energies are evaluated, a non-linear behaviour is observed and found to be in good agreement with theoretical values. Structural variations are observed for the variable alkali content. Optical absorption spectra confirms the near octahedral site symmetry for Mn^{2+} doped in LKB glasses. The EPR spectra exhibit well resolved intense characteristic signals of Mn^{2+} for $g = 2.02$. A non-linear behaviour is observed in spin-Hamiltonian parameters which confirms the MAE. An abrupt change at 20 mol% shows the anomaly character of the glass systems. FT-IR profile confirms the presence of BO_3 and BO_4 local structures in the glass systems. The corresponding vibrational bands showed shifts due to the change in the concentrations of Li and K. These changes clearly indicate the nature of MAE in the glass systems.

Acknowledgments

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