

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.

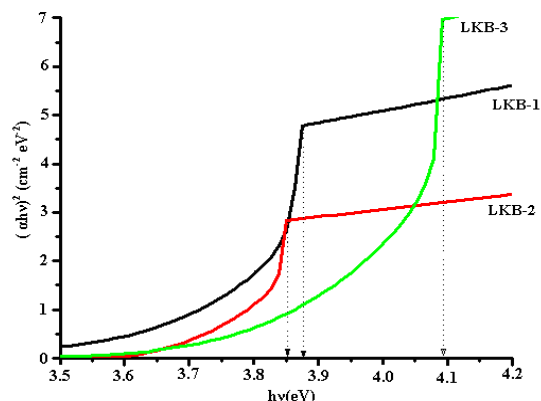


Figure 4: Direct bandgap energy diagram of Mn²⁺ doped LKB glasses

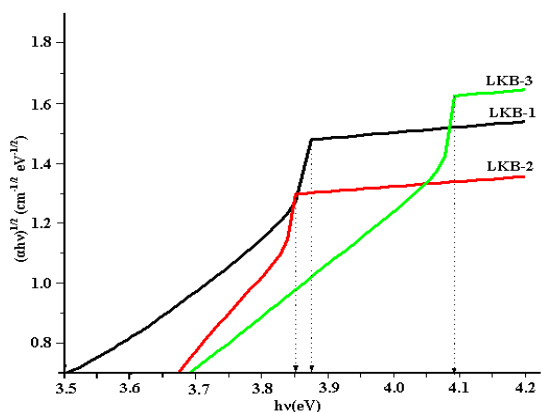


Figure 5: Indirect bandgap energy diagram of Mn²⁺ doped glasses

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 Li₂O 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.

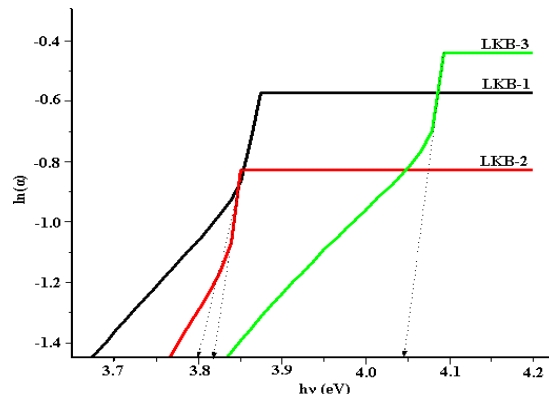


Figure 6: Urbach energy plots of Mn²⁺ doped LKB glasses

Table 3: Direct, Indirect band gap & Urbach energies of Mn²⁺ 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 Mn²⁺ doped LKB glasses are shown in Fig. 7.

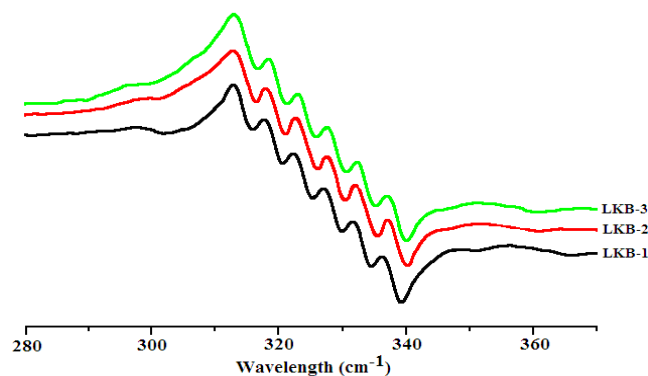


Figure 7: EPR spectra of Mn²⁺ doped glasses at room temperature

In general, EPR spectra of Mn²⁺ 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

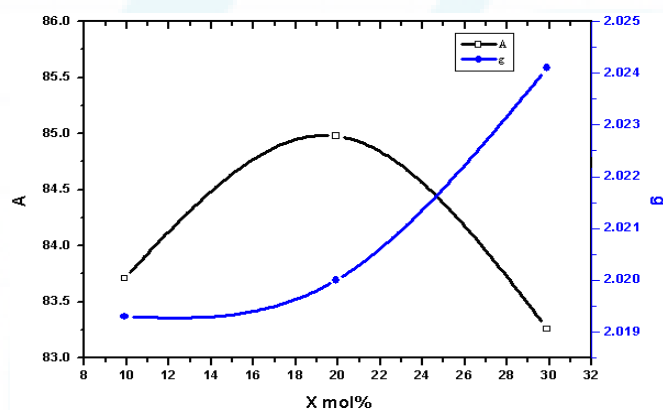


Figure 8: Composition dependence of g and A parameters of Mn^{2+} doped LKB glasses

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 $x Li_2O + (50-x) K_2O + 50 B_2O_3$ ($10 \leq x \leq 30$) LKB glasses are shown in Fig. 9.

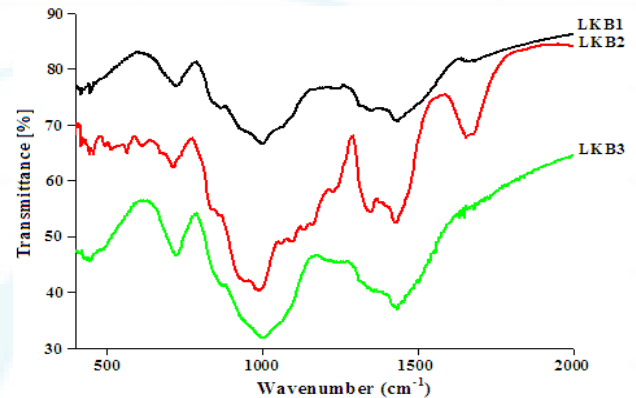


Figure 9: FT-IR spectra of Mn^{2+} doped LKB glasses

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 mol % of Mn^{2+} doped $x Li_2O + (50-x) K_2O + 50 B_2O_3$ ($10 \leq x \leq 30$) 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 Mn²⁺ doped in LKB glasses. The EPR spectra exhibit well resolved intense characteristic signals of Mn²⁺ 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 BO₃ and BO₄ 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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