Mixed alkali effect in borate glasses—EPR and optical absorption studies in $x\mathrm{Na_2O}-(30-x)\mathrm{K_2O}-70\mathrm{B_2O_3}$ glasses doped with $\mathrm{Mn^{2+}}$

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Abstract

The mixed alkali borate $x\mathrm{Na_2O}-(30-x)\mathrm{K_2O}-70\mathrm{B_2O_3}$ ($5 \leq x \leq 25$) glasses doped with 1 mol% of manganese ions were investigated using EPR and optical absorption techniques as a function of alkali content to look for 'mixed alkali effect' (MAE) on the spectral properties of the glasses. The EPR spectra of all the investigated samples exhibit resonance signals which are characteristic of the $\mathrm{Mn^{2+}}$ ions. The resonance signal at $g \cong 2.02$ exhibits a six line hyperfine structure. In addition to this, a prominent peak with $g \cong 4.64$, with a shoulder around $g \cong 4.05$ and 2.98, was also observed. From the observed EPR spectrum, the spin-Hamiltonian parameters g and A have been evaluated. It is interesting to note that some of the EPR parameters do show MAE. It is found that the ionic character increases with x and reaches a maximum around $x = 20$ and thereafter it decreases showing the MAE. The number of spins participating in resonance (N) at $g \cong 2.02$ decreases with x and reaches a minimum around $x = 20$ and thereafter it increases showing the MAE. It is also observed that the zero-field splitting parameter (D) increases with x, reaches a maximum around $x = 15$ and thereafter decreases showing the MAE. The optical absorption spectrum exhibits a broad band around $\sim 20{,}000\ \mathrm{cm^{-1}}$ which has been assigned to the transition $^6\mathrm{A_{1g}(S)} \rightarrow {}^4\mathrm{T_{1g}(G)}$. From ultraviolet absorption edges, the optical bandgap energies and Urbach energies were evaluated. It is interesting to note that the Urbach energies for these glasses decrease with x and reach a minimum around $x = 15$. The optical band gaps obtained in the present work lie in the range $3.28-3.40\ \mathrm{eV}$ for both the direct and indirect transitions. The physical parameters of all the glasses were also evaluated with respect to the composition.

1. Introduction

The mixed alkali effect (MAE) is one of the classic 'anomalies' of glass science [1–5]. Many properties of oxide glasses show non-linear behaviour exhibiting a minimum or maximum, as a function of alkali content, if one alkali ion is gradually replaced by another alkali ion, keeping the total alkali content constant. This behaviour is called the MAE, and is observed for properties associated with alkali ion movement such as electrical conductivity, ionic diffusion, dielectric relaxation and internal friction [1]. However, spectroscopic investigations of MAE are meagre, but they would be important and useful to gain insight into the microscopic origin of the MAE.

EPR and optical absorption are two such techniques. Manganese ions have been frequently used as paramagnetic probes for exploring the structure and properties of vitreous systems. Studies of the coordination, bonding characteristics and covalency state of transition metal ions in glasses are very helpful in understanding the structure of the glassy state. Changes in the chemical composition of glass may change the local environment of the transition metal ion incorporated into the glass, leading to ligand field changes,

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which may be reflected in the optical absorption and EPR spectra. Studies of transition metal ions in glasses by optical absorption and EPR may enable us to understand the structure of the glasses with varying composition.

Borate glasses are particularly interesting model systems as they exhibit a variety of structural changes with alkali content. A systematic study of the spectral characteristics in mixed alkali borate glasses would be useful in evolving a consistent understanding of the MAE in borate glasses. In the present investigations we have investigated sodium potassium borate glasses (hereafter referred as NaKB) doped with manganese ions using EPR and optical absorption techniques and the results obtained from these studies are discussed with respect to the composition of the mixed alkali elements.

2. Experimental

The starting materials M_2CO_3 (M = Na or K), H_3BO_3, MnO_2 used in the preparation of our NaKB glasses were of analar grade quality. Table 1 lists the batch composition in mol% of glasses studied in the present work. The chemicals were weighed accurately in an electronic balance, mixed thoroughly and ground to fine powder. The batches were then placed in porcelain crucibles and then melted in an electrical furnace in air at 1000 °C for 30 min. After heat treatment the melt was quenched at room temperature in air by pouring it onto a polished porcelain plate and pressing it with another porcelain plate. The glasses thus obtained were pink in colour. The glass formation was confirmed by recording the X-ray diffraction patterns with a Phillips type PW 1050 diffractometer, using Cu K_α radiation.

The EPR spectra were recorded at room temperature using a JEOL-FE-1X EPR spectrometer operating in the X-band frequency (≈ 9.200 GHz) with a field modulation frequency of 100 kHz. The magnetic field was scanned from 0 to 500 mT and the microwave power used was 5 mW. A powdered glass specimen of 100 mg was taken in a quartz tube for EPR measurements. The optical absorption spectra for the glass samples were recorded at 300 K on a Cintra (model GBC-40) UV–VIS spectrophotometer in the wavelength region 350–850 nm. The band position is measured digitally and the accuracy with which the peaks were measured is about ± 10 cm^{-1}.

Table 1
Composition of glasses studied in the present work

Glass code (x)	Glass system
5	$5Na_2O–25K_2O–69B_2O_3–1MnO_2$
10	$10Na_2O–20K_2O–69B_2O_3–1MnO_2$
15	$15Na_2O–15K_2O–69B_2O_3–1MnO_2$
20	$20Na_2O–10K_2O–69B_2O_3–1MnO_2$
25	$25Na_2O–5K_2O–69B_2O_3–1MnO_2$

2.1. Physical properties of manganese doped mixed alkali borate glasses

The density (D) of the glass samples at room temperature was measured by the Archimedes principle using a sensitive micro balance with xylene as the immersion liquid. The mean atomic volume (V) of each glass was obtained from the values of densities (D) and mean atomic weights. The number of manganese ions (N) was determined from the glass composition and its density value. The refractive index (n_d) of the glass was measured with an Abbe Refractometer at sodium wavelength ($\lambda = 5893$ Å).

The dielectric constant (ϵ) was calculated from the refractive index of the glass using [6].

$$\epsilon = n_d^2 \tag{1}$$

The reflection loss from the glass surface was computed from the refractive index by using the Fresnel's formula as shown below [7]

$$R = \left[\frac{(n_d - 1)}{(n_d + 1)} \right]^2 \tag{2}$$

The molar refractivity R_M for each glass was evaluated using [8]

$$R_M = \left[\frac{(n_d - 1)}{(n_d + 2)} \right] \frac{M}{D} \tag{3}$$

where M is the average molecular weight and D is the density in gm cm^{-3}.

The electronic polarizability α_e was calculated using the formula [9]

$$\alpha_e = \frac{3(n_d^2 - 1)}{4\pi N(n_d^2 + 2)} \tag{4}$$

where N is the number of manganese ions per unit volume.

The polaron radius and inter-ionic separation were calculated using the formulae [10]

$$r_p = \frac{1}{2} \left(\frac{\Pi}{6N} \right)^{(1/3)} \tag{5}$$

and

$$r_i = \left(\frac{1}{N} \right)^{(1/3)} \tag{6}$$

2.2. Optical basicity of the glass (Λ_{th})

The optical basicity of an oxide glass will reflect the ability of the glass to donate negative charge to the probe ion [11]. Duffy and Ingram [12] reported that the optical basicity can be predicted from the composition of the glass and the basicity moderating parameters of the various cations present. The theoretical values of optical basicity of

Table 2
Certain physical parameters of manganese ions doped in NaKB glasses studied in the present work at room temperature

S.No.	Physical property	Glass code				
		$x = 5$	$x = 10$	$x = 15$	$x = 20$	$x = 25$
1	Average molecular weight	83.383	81.778	80.161	78.709	76.939
2	Density, D (g/cc)	2.362	2.569	2.601	2.575	2.653
3	Refractive index, n_D	1.518	1.515	1.511	1.506	1.509
4	Molar refractivity, R_M (cm^{-3}) (± 0.005)	10.697	10.302	9.232	9.081	8.659
5	Mean atomic volume, V (g/cm^3/atom) (± 0.025)	0.0806	0.0780	0.0704	0.0698	0.0662
6	Optical dielectric constant, (ϵ) (± 0.005)	2.304	2.295	2.283	2.268	2.277
7	Electronic polarisability, $\alpha_e \times 10^{-24}$(ions/cm^3) (± 0.005)	4.239	4.083	3.658	3.598	3.432
8	Concentration, $N \times 10^{22}$(ions/cm^3) (± 0.005)	1.706	1.763	1.955	1.971	2.077
9	Optical basicity	0.4037	0.3992	0.3947	0.3903	0.3860
10	Ionic radius, r_P (Å) (± 0.005)	1.565	1.548	1.495	1.491	1.466
11	Inter-ionic distance, r_i (Å) (± 0.005)	3.884	3.842	3.712	3.702	3.638

the glass can be estimated using the formula [12]

$$\Lambda_{th} = \sum_{i=1}^{n} \frac{Z_i r_i}{2\gamma_I} \qquad (7)$$

where n is the total number of cations present, Z_i is the oxidation number of the ith cation, r_i is the ratio of number of ith cations to the number of oxides present and γ_i is the basicity moderating parameter of the ith cation. The basicity moderating parameter γ_i can be calculated [12] from the following equation

$$\gamma_i = 1.36(x_i - 0.26) \qquad (8)$$

where x_i is the Pauling electronegativity [13] of the cation. The theoretical values of optical basicity (Λ_{th}) were calculated for all the glass samples and are listed in Table 2. It is observed that the optical basicity of the glasses decreases linearly with x. It is also observed that, the physical parameters like average molecular weight, refractive index, molar refractivity, mean atomic volume, electronic polarisability, polaron radii, inter-ionic distances evaluated for the glasses studied in the present work, decreases linearly with x, and are also included in Table 2.

3. Results and discussion

3.1. X-ray diffraction

The X-ray diffraction is a quite useful technique because it is possible to detect readily crystals in a glassy matrix if the crystals are of dimensions greater than typically 100 nm [14]. The X-ray diffraction pattern of an amorphous material is distinctly different from that of crystalline material and consists of a few broad diffuse haloes rather than sharp rings. All the samples were tested and the results showed the absence of crystalline characteristics. Fig. 1 shows the typical X-ray diffraction patterns for these compositions
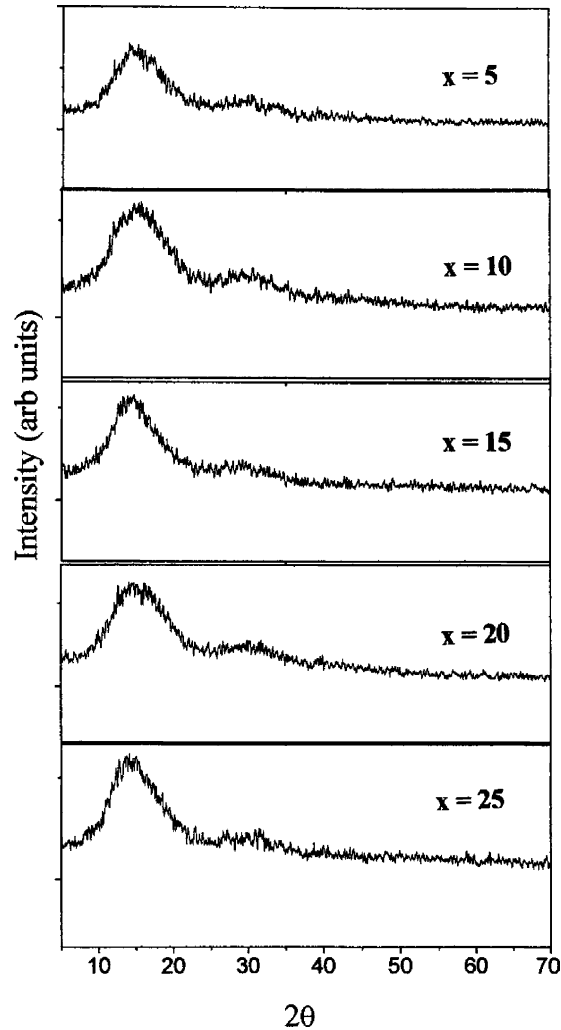

Fig. 1. X-ray diffraction pattern for different mixed alkali borate glasses xNa$_2$O$-(30 - x)$K$_2$O-69B$_2$O$_3-1$ MnO$_2(5 \le x \le 25)$ at room temperature.

(Table 1). The patterns obtained did not reveal any crystalline phase in the glass.

3.2. EPR studies

No EPR signal was detected in the spectra of undoped glasses. When manganese ions were introduced to NaKB glasses (Table 1), the EPR spectra of all the investigated samples exhibit resonance signals due to Mn^{2+} ($3d^5$:$^6S_{5/2}$) ions entering the matrix as paramagnetic species. The spectrum of Mn^{2+} ions exhibits a broad resonance consisting of a sextet, at $g \cong 2.02$ with a total peak width of 480 G and is shown in Fig. 2. In addition to this, a prominent peak with $g \cong 4.64$, and shoulders around $g \cong 4.05$ and 2.98 were also observed. The EPR spectra of these samples are similar to those reported for manganese ions [15–24] in various glass systems.

The EPR spectra of manganese ions in NaKB glasses with different compositions of mixed alkalis at 300 K are shown in Fig. 2. The resonance signal at $g \cong 2.02$ shows a six line hyperfine structure (hfs) which is due to the interaction of electron spin of manganese ions with its own nuclear spin

$I = 5/2$. The ability to observe the ^{55}Mn hfs has two tangible benefits: (1) it generally allows unambiguous assignments of positions of complex resonance lines to manganese and (2) the magnitude of hyperfine splitting constant provides a measure of the covalent bonding between Mn^{2+} ions and its surrounding ligands [25,26]. Their relative intensities vary with glass structure and composition.

In case of d^5 transition metal ions, it is known that axial distortion of octahedral symmetry gives rise to three Kramer's doublets $|\pm 5/2\rangle$, $|\pm 3/2\rangle$ and $|\pm 1/2\rangle$ [27]. Application of Zeeman field lifts the spin degeneracy of the Kramer's doublets. As the crystal field splitting is normally much greater than the Zeeman field, the resonances observed are due to transitions within the Zeeman field split Kramer's doublets. The resonances at $g \approx 2.98$ and 4.64 can be attributed to the rhombic surroundings of the Mn^{2+} ions. The resonance at $g \approx 2.0$ is due to the Mn^{2+} ions in an environment close to octahedral symmetry and is known to arise from the transition between the energy levels of the lower doublet, while the resonances at $g \approx 2.98$ and 4.64 arise from the transition between the energy levels of middle Kramer's doublet.
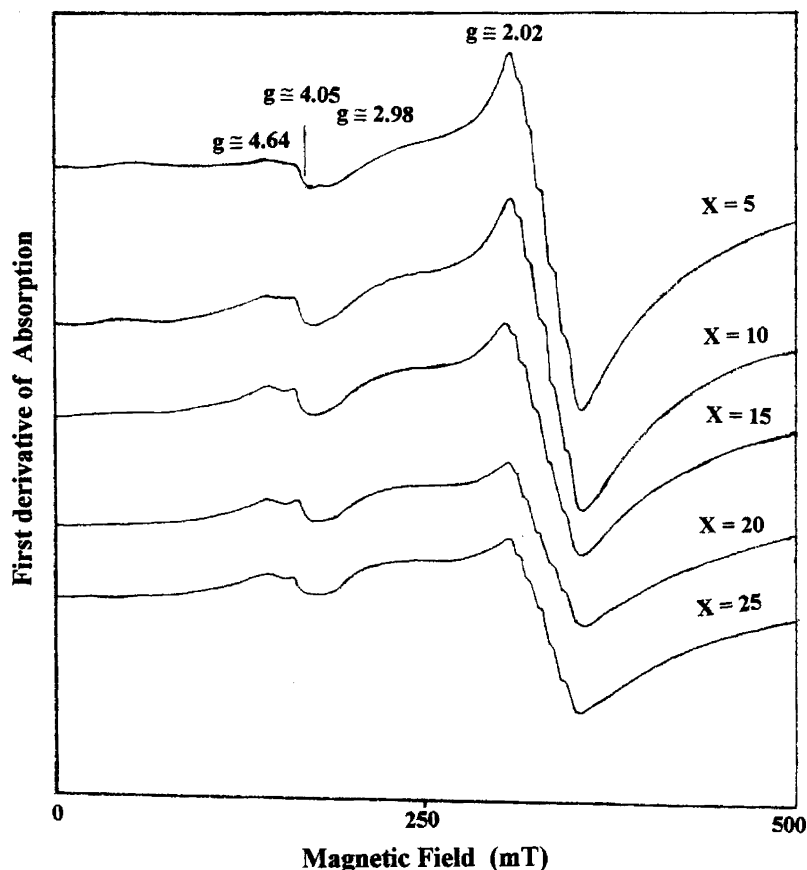

Fig. 2. EPR spectra of manganese in the mixed alkali borate glasses $xNa_2O–(30 - x)K_2O–69B_2O_3–1$ $MnO_2(5 \leq x \leq 25)$ at room temperature.

Table 3
The hyperfine splitting (A), g factor and zero-field splitting (D) values for 1 mol% Mn^{2+} ions in NaKB glasses at room temperature with x

Glass code (x)	g	Δg	A_{pp} (10^{-4} cm^{-1})	A_{tt} (10^{-4} cm^{-1})	A (10^{-4} cm^{-1})	$D \times 10^{-4}$ (10^{-4} cm^{-1})
5	2.019	−0.0167	71	82	76.5	221
10	2.019	−0.0167	71	85	78.0	236
15	2.027	−0.0247	76	90	83.0	280
20	2.027	−0.0247	79	89	84.0	255
25	2.027	−0.0247	76	82	79.0	222

(The errors in g and A values are ± 0.001 and $\pm 2 \times 10^{-4}$ cm^{-1}, respectively).

Table 3 gives some typical values of the hfs (A) and g-values for 1 mol% of Mn^{2+} ions in NaKB glass at room temperature. It is apparent from different average values of A measured from peak to peak, A_{pp}, and trough to trough, A_{tt}, that the individual lines are strain broadened, leading to an asymmetry in the absorption spectrum [28]. The first derivative spectrum as a consequence, shows larger values of A, when measured trough to trough, rather than peak to peak. An overall average was calculated from

$$A_{avg} = [(\Delta_{Opp} + \Delta_{Ott})/5 + (\Delta_{Mpp} + \Delta_{Mtt})/3 + (\Delta_{Ipp} + \Delta_{Itt})]/6 \quad (9)$$

where Δ_{Opp} and Δ_{Ott} represent the differences between the first and sixth peak positions, measured peak to peak and trough to trough, respectively. Δ_{Mpp} and Δ_{Mtt} represents difference in positions between second and fifth peaks and Δ_{Ipp} and Δ_{Itt} between second and third peaks. It is interesting to note that, in all of the glass samples, $\Delta_{Opp}/5 \approx \Delta_{Mpp}/3 \approx \Delta_{Ipp}$ and $\Delta_{Ott}/5 \approx \Delta_{Mtt}/3 \approx \Delta_{Itt}$. This indicates that the g-value in each case is well behaved [28].

The Mn^{2+} signals are similar in all the glasses studied so far, the major difference appearing in the magnitude of the hyperfine splitting. Van Wieringen [25] has noted that the strength of the hyperfine splitting depends on the matrix into which the ion is dissolved and is mainly determined by the electronegativity of the neighbours. This means a qualitative measure of the covalency of the bonding in the matrix which can be determined from the value of A; the smaller the splitting, the more covalent the bonding of the anion. It was also noted [25] that the g-value for the hyperfine splitting was indicative of the nature of bonding in the glass. If the g-value shows a negative shift with respect to 2.0023, then the bonding is ionic and conversely, if the shift is positive, then the bonding is more covalent in nature. In the present work, from the measured negative shift in the g-value, with respect to 2.0023, it is apparent that the Mn^{2+} ion is in an ionic environment [25]. It is interesting to note that the hyperfine splitting constant increases with x, and reaches a maximum around $x = 20$ and thereafter it decreases showing the MAE in these glasses as shown in Fig. 3. This indicates that, the ionic character increases with x, reaches a maximum around $x = 20$ and thereafter it decreases with x showing the MAE in these glasses.

3.3. Calculation of number of spins (N) participating in resonance

The number of spins participating in resonance can be calculated by comparing the area under the absorption curve with that of a standard ($CuSO_4 \cdot 5H_2O$ in this study) of known concentration. Weil et al. [29] gave the following expression
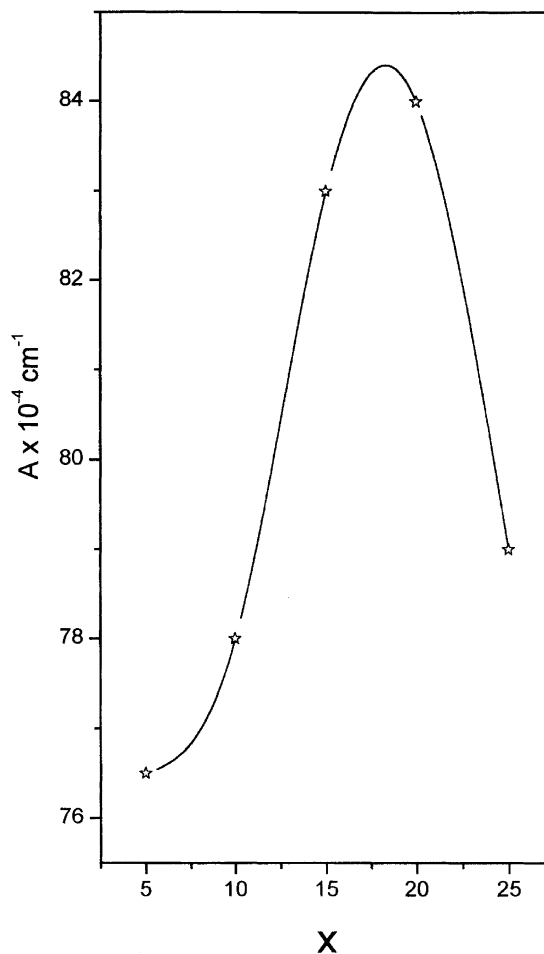

Fig. 3. The variation of hyperfine splitting constant with x in the mixed alkali borate glasses $xNa_2O-(30 - x)K_2O-69B_2O_3-1MnO_2$ $(5 \leq x \leq 25)$ at room temperature.

which includes the experimental parameters of both sample and standard

$$N = \frac{A_x(\text{Scan}_x)^2 G_{\text{std}}(B_m)_{\text{std}}(g_{\text{std}})^2[S(S+1)]_{\text{std}}(P_{\text{std}})^{1/2}}{A_{\text{std}}(\text{Scan}_{\text{std}})^2 G_x(B_m)_x(g_x)^2[S(S+1)]_x(P_x)^{1/2}} [\text{Std}]$$

(10)

where A is the area under the absorption curve which can be obtained by double integrating the first derivative EPR absorption curve, scan is the magnetic field corresponding to unit length of the chart, G is the gain, B_m is the modulation field width, g is the g factor, S is the spin of the system in its ground state. P is the power of the microwave. The subscripts x and 'std' represent the corresponding quantities for Mn^{2+} glass sample and the reference ($CuSO_4 \cdot 5H_2O$), respectively. Fig. 4 shows the number of spins participating in resonance at $g \approx 2.02$ resonance line for 1 mol% of manganese ions in NaKB glasses as a function of alkali content at room temperature. It is quite interesting to note that the number of spins participating in resonance decreases with x, reaches a minimum around $x = 20$ and thereafter increases showing the MAE. These changes are due to structural changes with alkali content.

Further, it can be observed from the EPR spectra (Fig. 2) that $g \approx 2.02$ resonance is very intense compared to those at $g \appro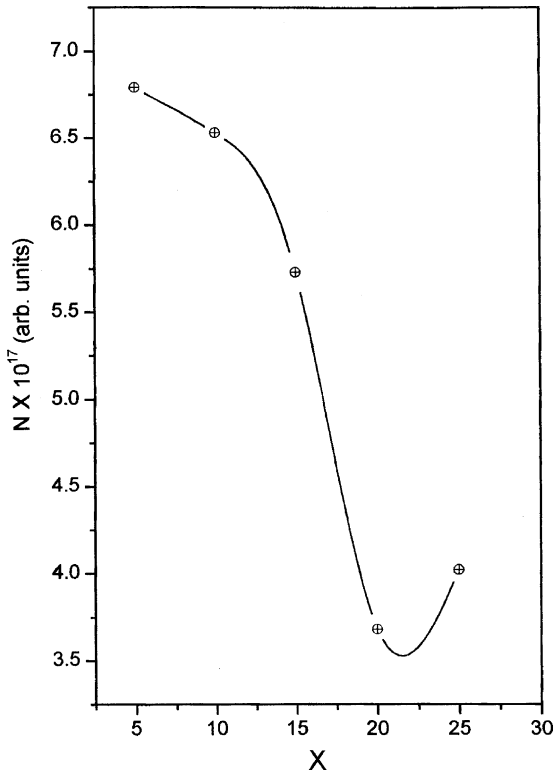x 2.98$ and 4.64 indicating that the Mn^{2+} ions predominantly occupy octahedral sites (i.e. $g \approx 2.02$). Similar observations have also been reported by Harris [30] in fluoride glasses and Barnier et al. [31] in $GaS_{3/2}-GeS_2-MnS$ glasses.

In the present work, it is also interesting to note that the intensity of the EPR signal (corresponding to $g \approx 2.02$) changes with x and reaches a minimum at $x = 20$. This indicates that the site symmetry around some of the Mn^{2+} ions is affected (lowered) by changing x, which shows that the structural changes taking place with composition are reflected in the site symmetry and the intensity of the resonance. Corresponding intensity changes are expected in the resonances at the other g-values too. However, accurate estimates of the number N (i.e. intensity) could not be made due to lower intensities.

3.4. Calculation of zero-field splitting parameter (D) from EPR spectra from the allowed hyperfine lines

The intensity of hyperfine lines can be used to calculate the zero-field splitting parameter (D) from the ratio of allowed hyperfine lines (corresponding to the selection rule $\Delta m = 0$). Allen [32] provided a method of estimating D from the intensities of the allowed hyperfine lines of the central sextet. In the present case the zero-field splitting parameter (D) was evaluated by using the expressions given
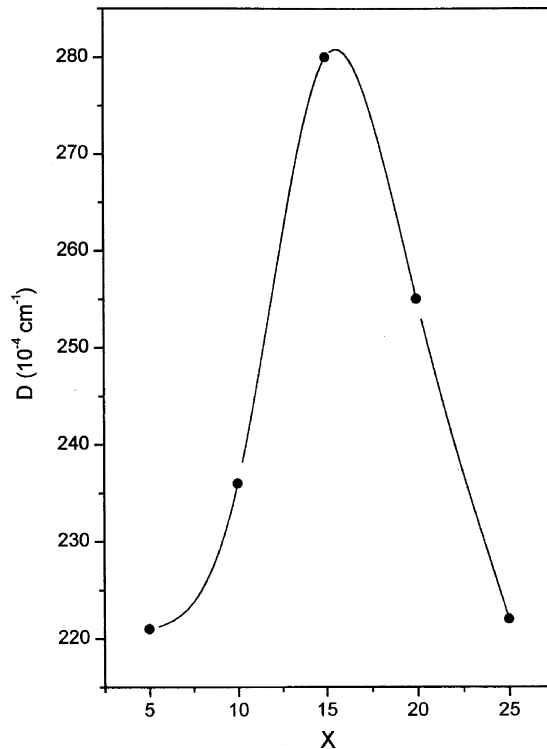

Fig. 4. The variation of number of spins (N) with x in different mixed alkali borate glasses $x\text{Na}_2\text{O}-(30-x)\text{K}_2\text{O}-69\text{B}_2\text{O}_3-1\text{MnO}_2$ ($5 \leq x \leq 25$) at room temperature.
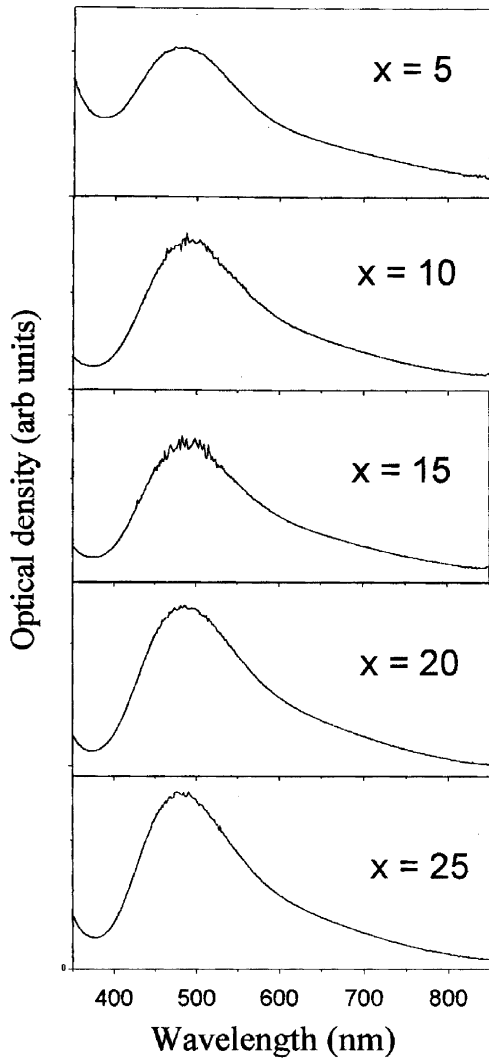

Fig. 5. The variation of Zero-field splitting parameter (D) with x in the mixed alkali borate glasses $x\text{Na}_2\text{O}-(30-x)\text{K}_2\text{O}-69\text{B}_2\text{O}_3-1\text{MnO}_2$ ($5 \leq x \leq 25$) at room temperature.

4. Optical absorption studies

Fig. 6 shows the optical absorption spectra of manganese ions in NaKB glasses with x. From the figure it is seen that the absorption spectrum shows a single broad band. In a cubic crystalline field of low to moderate strength, the five d electrons of Mn^{2+} ion are distributed in the t_{2g} and e_g orbitals, with three in the former and two in the latter. Thus, the ground state configuration is $(t_{2g})^3 (e_g)^2$. This configuration gives rise to the electronic states, $^6A_{1g}$, $^4A_{1g}$, ^4E_g, $^4T_{1g}$, $^4T_{2g}$, and to a number of doublet states of which $^6A_{1g}$ lies lowest according to Hund's rule. Since all the excited states of Mn^{2+} ion (belonging to d^5 configuration) will be either quartets or doublets, the optical absorption spectra of Mn^{2+} ions will have only spin forbidden transitions. In the present case, the band observed $\sim 20,000$ cm^{-1} can be assigned to the transition $^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$. The band positions reported for the different mixed alkali NaKB glasses corresponding to $^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$ transition are also presented in Table 4. From Table 4, it is observed that the band position shifts clearly to lower energy side up to $x = 15$ reaching a minimum and thereafter increases to higher energy side showing the MAE. The only other optical absorption experiments in mixed alkali glasses are by Turner et al., Sakka et al., Hosono et al., on Cu and Ni doped silicate glasses [33–35] and by Ahmed et al., on Cu doped borate glasses [36]. However, they did not report the band positions but concluded that the effect is small.

4.1. Optical band gaps

The study of the fundamental absorption edge in the UV-region is a useful method for the investigation of optical transitions and electronic band structure in crystalline and non-crystalline materials. There are two types of optical transitions that can occur at the fundamental absorption edge of crystalline and non-crystalline materials. They are direct and indirect transitions. In both the cases, electromagnetic waves interact with the electrons in the valence band, which are raised across the fundamental gap to the conduction band. Davis and Mott [37] gave the following forms of absorption co-efficient $\alpha(\nu)$ as a function of photon energy for direct and

Fig. 6. Optical absorption spectra of the mixed alkali borate glasses xNa$_2$O$-(30-x)$K$_2$O-69B$_2$O$_3-1$MnO$_2$ $(5 \le x \le 25)$ at room temperature.

by Allen [32] and are listed in Table 3. It is quite interesting to note that the zero-field splitting parameter (D) increases with x and reaches a maximum around $x = 15$ and thereafter decreases showing the MAE and is shown in Fig. 5.

Table 4
Observed band positions, optical band gap and Urbach energies for Mn^{2+} ions in NaKB glass matrices with x

Glass code (x)	Transition from $^6A_{1g}(S) \rightarrow$	Observed band position (nm)	Observed band position (cm^{-1})	Optical band gap		Urbach energy ΔE (eV)
				Indirect (eV)	Direct (eV)	
5	$^4T_{1g}(G)$	487.5	20507	3.28	3.33	0.344
10	$^4T_{1g}(G)$	490.6	20377	3.38	3.39	0.233
15	$^4T_{1g}(G)$	494.3	20237	3.29	3.35	0.200
20	$^4T_{1g}(G)$	487.0	20528	3.38	3.39	0.277
25	$^4T_{1g}(G)$	481.2	20775	3.35	3.40	0.300

indirect transitions. For direct transitions,

$$\alpha(\nu) = B(h\nu - E_{opt})^n/h\nu \qquad (11)$$

where $n = 1/2$ for allowed transition, B is a constant and E_{opt} is direct optical band gap. For indirect transitions,

$$\alpha(\nu) = B(h\nu - E_{opt})^n/h\nu \qquad (12)$$

where $n = 2$ for allowed transitions and E_{opt} is the indirect optical band gap. Using the above two equations, by plotting $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ as a function of photon energy $\hbar\nu$, one can find the optical energy band gap (E_{opt}) for indirect and direct transitions, respectively. The respective values of E_{opt} are obtained by extrapolating to $(\alpha h\nu)^{1/2} = 0$ for indirect transitions and $(\alpha h\nu)^2 = 0$ for direct transitions.

In order to examine the optical band gap energy for these mixed alkali glasses the optical absorption spectra were also recorded in the near ultra violet region. The main feature of the absorption edge of amorphous materials is an exponential increase of the absorption coefficient $\alpha(\nu)$ with photon energy $h\nu$ in accordance with the empirical relation [38]

$$\alpha(\nu) = \alpha_0 \exp(h\nu/\Delta E) \qquad (13)$$

where α_0 is a constant, ΔE is the Urbach energy which indicates the width of the band tails of the localized states and ν is the frequency of the radiation. The excitation levels at the absorption edges are determined by the random electric fields due to either the lack of long range order or the presence of defects [37,39]. Plots were drawn between $(\alpha h\nu)^{1/2}$, $(\alpha h\nu)^2$ vs $h\nu$ and are shown in Figs. 7 and 8, respectively. From these plots the optical band gap energies were calculated and are presented in Table 4. It is observed that the optical band gap energy increases with x and reaches a maximum around $x = 15$ and thereafter it decreases showing the MAE. Plots were also drawn between $\ln(\alpha)$ vs $h\nu$. From these plots and the slopes, the Urbach energy was calculated. It is interesting to note that the Urbach energies for these glasses decrease with x and reach a minimum at $x = 15$. Thereafter, they slightly increase showing the MAE in the NaKB glasses. The optical energy band gap and Urbach energies studied in the present work are listed in Table 4. The optical band gap energy is obtained by extrapolating the linear region of the curve to the $h\nu$ axis. The optical band gap obtained in the present work varies
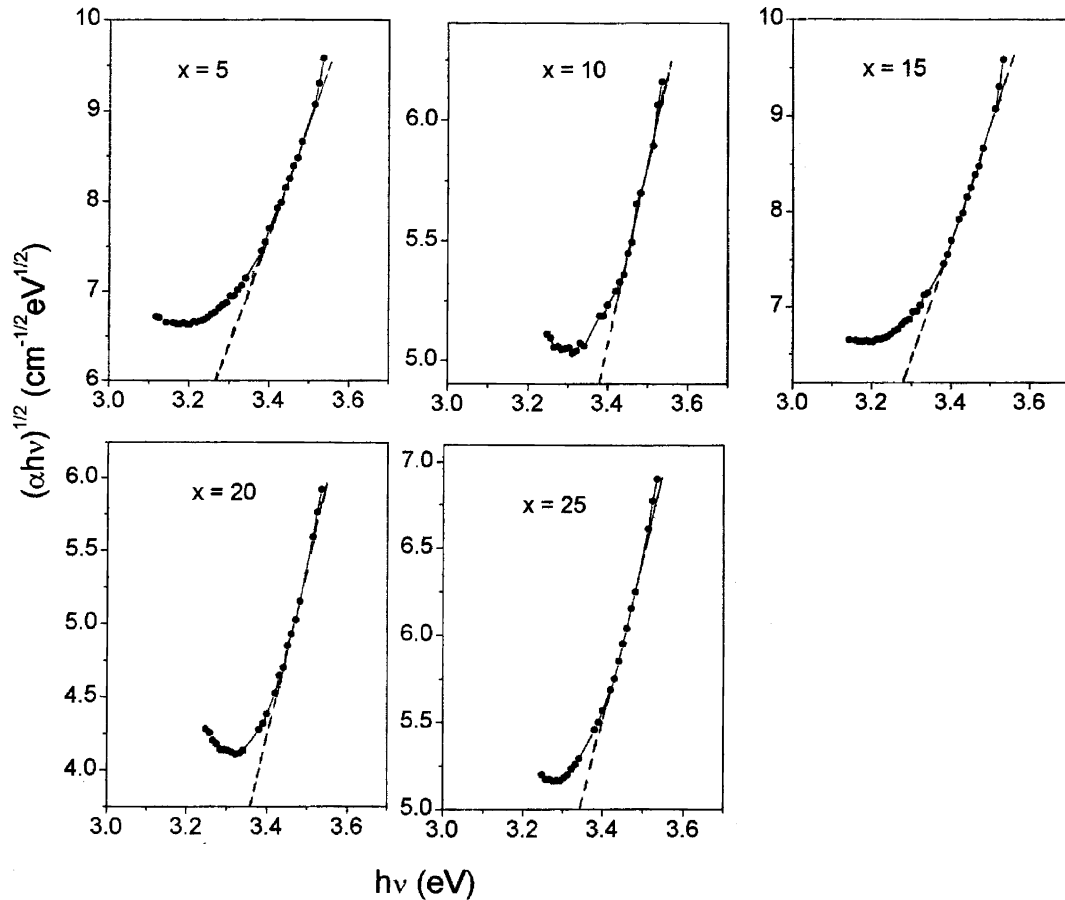

Fig. 7. Plots corresponding $(\alpha h\nu)^{1/2}$ vs $h\nu$ for the mixed alkali borate glasses xNa$_2$O$-(30 - x)$K$_2$O-69B$_2$O$_3-1$MnO$_2$ ($5 \le x \le 25$) at room temperature.

Fig. 8. Plots corresponding $(\alpha h\nu)^2$ vs $h\nu$ for the mixed alkali borate glasses $x\text{Na}_2\text{O}-(30-x)\text{K}_2\text{O}-69\text{B}_2\text{O}_3-1\text{MnO}_2$ ($5 \leq x \leq 25$) at room temperature.
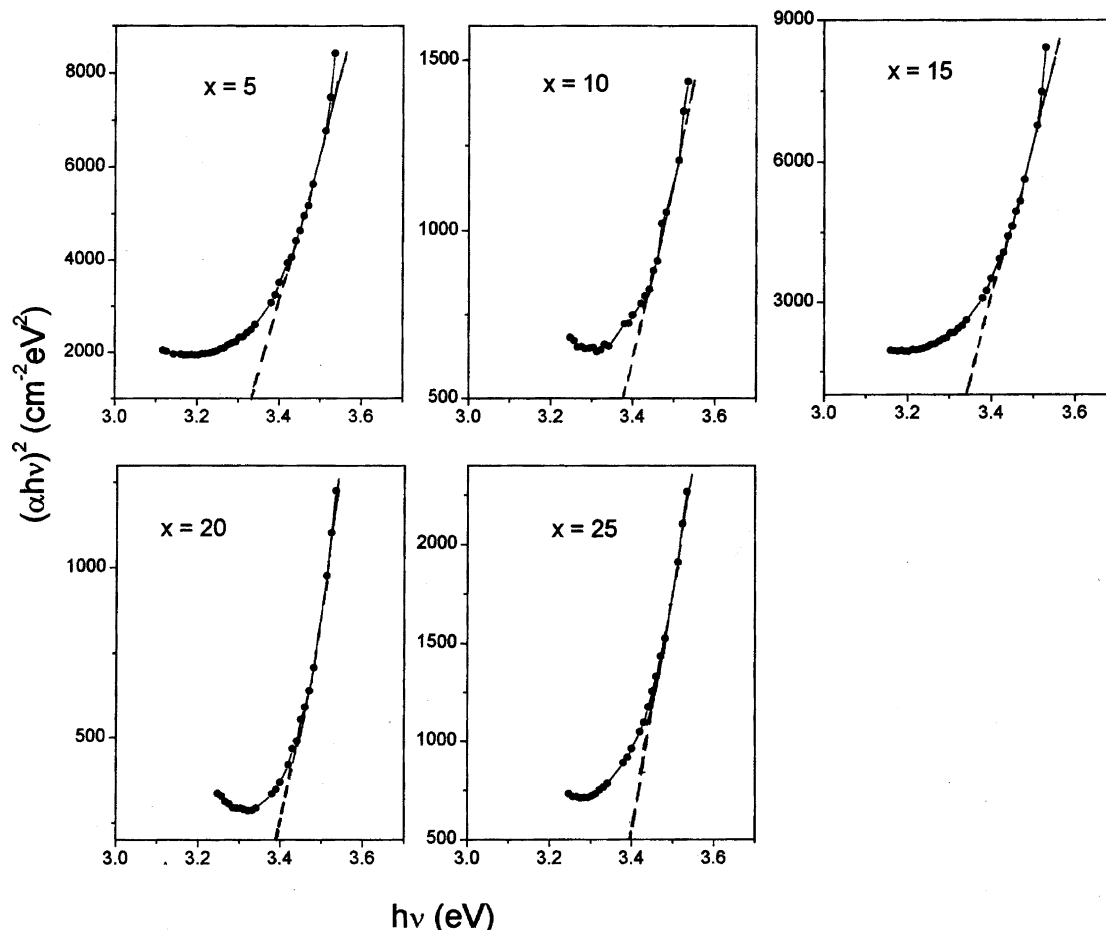
from 3.28 to 3.40 eV for both the direct and indirect transitions which is of the same order expected for borate glasses.

5. Conclusions

1. Some of the EPR parameters like number of spins, zero-field splitting parameter, hyperfine splitting constant do show the MAE type behaviour if one alkali gradually replaces the other in the mixed alkali borate glasses.

2. In all the investigated samples the EPR spectra exhibit resonance signals which are characteristic of the Mn^{2+} ions. The resonance signal at $g \cong 2.02$ shows a six line hfs, due to the interaction of electron spin (with $S = 5/2$) of manganese ions with its own nuclear spin $I = 5/2$. In addition to this, a prominent peak with $g \cong 4.64$, and shoulders around $g \cong 4.05$ and 2.98 were also observed. The resonance signal at $g \cong 2.02$ is due to Mn^{2+} ions in an environment close to octahedral symmetry, whereas

the resonances at $g \cong 4.64$, 4.05 and 2.98 are attributed to the rhombic surroundings of the Mn^{2+} ions.

3. The ionic character increases with x and reaches a maximum around $x = 20$ and thereafter it decreases showing the MAE.

4. The number of spins (N) participating in resonance decreases with replacement of one alkali by the other and reach a minimum around $x = 20$ showing the MAE.

5. It is also observed that the zero-field splitting parameter (D) increases with x, reaches a maximum around $x = 15$ and thereafter decreases showing the MAE.

6. The physical parameters like average molecular weight, refractive index, molar refractivity, mean atomic volume, electronic polarisability, polaron radii, inter-ionic distances evaluated for the glasses studied in the present work, decrease linearly with x.

7. The optical absorption spectrum exhibits a single broad band corresponding to the transition $^6\text{A}_{1g}(\text{S}) \rightarrow {}^4\text{T}_{1g}(\text{G})$ and the band position shifts with x showing a minimum around $x = 15$ (a signature of MAE).

8. From ultraviolet absorption edges the optical bandgap energies and Urbach energies were evaluated.

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