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RESEARCH ARTICLE

SPECTROSCOPIC STUDIES OF MANGANESE IONS IN MIXED ALKALI BORATE GLASSES

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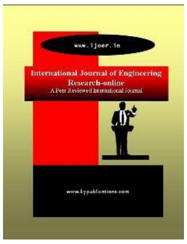

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ABSTRACT

The optical absorption and IR spectra of Na_2O/Li_2O mixed alkali borate glasses doped with MnO have been carried out. The analysis of the results indicated that there is a decreasing proportion of manganese ions that oxidize from Mn^{2+} state to Mn^{3+} state as the concentration of Na_2O is increased from 0 to 40 mol%.

1. Introduction

The mixed alkali effect in the glass materials has been the subject of study in the recent years. Many properties of glasses show nonlinear behaviour of exhibiting a minimum or maximum, as a function of alkali content, if one of the alkali ions is gradually replaced by another alkali keeping total alkali content constant. This behaviour is called mixed alkali effect. The general formula for mixed alkali oxide glass is $y[x.A_2O + (1-x) B_2O] + (1-y)$ glass former, where A and B are alkalis. The extent of departure from linearity, the direction of variation (positive or negative) depends on the property examined and the glass system. The behavior of mixed alkali effect is independent of glass forming oxides. It is being observed in silicates, borates, phosphates, germanates, tellurites, boro alluminate, alumino silicates, borotellurate etc., glasses. It is also observed that properties related to cationic movement are more sensitive to mixed alkali effect [1-3].

Alkali oxy borate glasses like $Li_2O–Na_2O–B_2O_3$ glasses doped with different transitional metal ions ions like Fe^{2+}, Cu^{2+}, Ti^{4+}etc, find variety of applications as electronic materials, in radiation dosimetry and in a number of other technological fields. [4-12].

Among various transition metal ions, manganese ion, is an interesting ion because it exists in different valence states in different glass matrices, for example in silicate and germanate glasses it exists in Mn^{2+} with both octahedral and tetrahedral coordination [13]. Further, among different manganese ions, Mn^{2+} and Mn^{3+} are well known paramagnetic ions and Mn^{2+} and Mn^{4+} are identified as luminescence activators [14]. Further, it is also quite likely for manganese ions to have link with borate groups; strengthen its structure and may raise the chemical resistance of the glass. The content of manganese in different forms in different valence states exist in the glass depends on the quantitative properties of modifiers and glass formers, size of the ions in the glass structure, their field strength, mobility of the modifier cation etc. Hence, the connection between the state and the position of the manganese ion and the physical properties of the glass is expected to be highly interesting.

Mn^{2+} has the electronic configuration $3d^5$ which corresponds to a half filled d shell. Most Mn^{2+} complexes are octahedral and have a high spin arrangement with five unpaired electrons [15]. In extensive studies are available on the spectroscopic properties of manganese ion in various inorganic glass systems. These ions subsist in different surroundings (ionic, covalent) in glass matrices. It is quite likely that these manganese ions to exist in Mn^{2+} and Mn^{3+} states in alkali oxy borate glass network. The most probable local structure likely to occur for Mn^{3+} in these glasses is as a MnO_6 octahedron entwined with a BO_4 tetrahedron $MnBO_9$ where all the oxygens are bridging. The presence of such complexes obviously increases the stability of the glass network. Even though a number of recent investigations are available on the environment of manganese ions in a variety of inorganic glass systems are available [16-20].

2. Experimental

The glasses used for the present study are prepared by the melting and quenching techniques [21-23]. Batch materials to produce 10 g of each glass were accurately weighed, thoroughly mixed in an agate mortar and melted in a platinum crucible. Appropriate amounts (all in mol %) of reagent grades of H_3BO_3, Na_2CO_3, Li_2CO_3 and MnO powders were thoroughly mixed in an agate mortar and melted in a thick walled platinum crucible in the temperature range 900-950°C using a PID temperature controlled furnace. The glasses were melted in a thick walled platinum crucible for an hour till a bubble free liquid was formed. The resultant melt was poured on a rectangular brass mould (having smooth polished inner surface) held at room temperature and subsequently annealed at 200°C in another furnace. The weight of the glass obtained always agreed with that anticipated in the batch, with an error of 0.2 to 0.5 % wt loss in each case. The results indicate that the actual glass compositions are essentially equal to those based on the glass batch. The glasses were then ground and optically polished. The approximate final dimensions of the glasses used for present study are 1 cm x 1 cm x 0.2 cm.

In this work, an attempt is made to have a broad understanding over the mixed alkali effect on spectroscopic properties of a series of Li_2O-Na_2O-B_2O_3 glasses containing a fixed concentration of MnO. Measurements taken are optical absorption and IR spectra. Within the glass forming region of Li_2O-Na_2O-B_2O_3, the following compositions are chosen for the present study:

L_0: $0.0Li_2O$–$40Na_2O$–$59.5B_2O_3$: 0.5MnO
L_1: $10Li_2O$–$30Na_2O$–$59.5B_2O_3$: 0.5MnO
L_2: $20Li_2O$–$20Na_2O$–$59.5B_2O_3$: 0.5MnO
L_3: $30Li_2O$–$10Na_2O$–$59.5B_2O_3$: 0.5MnO
L_4: $40Li_2O$–$0.0Na_2O$–$59.5B_2O_3$: 0.5MnO (all are in mol %).

The density (d) of the glasses was determined by the standard principle of Archimedis' using o-xylene (99.99 % pure) as the buoyant liquid. A direct reading balance (capacity 100 g, readability 0.1 mg) was used for weighing. The bulk glass was suspended on a very thin copper strand was set in the immersion liquid container and weighed in the liquid and air. The optical absorption spectra of the glasses were recorded at room temperature in the spectral wavelength range covering 300–2100 nm with a spectral resolution of 0.1 nm using JASCO Model V-670 UV–vis–NIR spectrophotometer. Infrared transmission spectra were recorded on a with a resolution of 0.1 cm^{-1} in the spectral range 400–2000 cm^{-1} using potassium bromide pellets (300 mg) containing pulverized sample (1.5 mg). These pellets were pressed in a vacuum die at ~680MPa. The spectra were recorded on Jasco-FT/IR-5300 spectrophotometer.

3. Results

3.1 Physical Parameters

From the measured values of density, d and calculated average molecular weight $\overline{M}$, various physical parameters such as manganese ion concentration, N_i, inter-ionic distance, (r_i), polaron radius, (r_p), field strength, (F_i) and molar volume, (M) which are useful for understanding the physical properties of these glasses are evaluated and presented in Table 1

Table 1

Summary of data on various physical parameters of $Li_2O–Na_2O–B_2O_3$: MnO glasses

Sample	Density (d) (g/cm^3)	Average molecular weight	N_i (10^{21}, ions/cm^3)	R_i (°A)	R_p (°A)	Fi (10^{15} cm^{-2})	Molar volume
L_0	2.481	66.75	1.17	9.45	3.82	2.05	26.90
L_1	2.459	63.54	1.22	9.36	3.77	2.11	25.84
L_2	2.448	60.33	1.28	9.21	3.71	2.18	24.64
L_3	2.412	57.12	1.33	9.09	3.66	2.23	23.67
L_4	2.391	53.91	1.40	8.95	3.60	2.31	22.55

3.2 Optical absorption spectra

The optical absorption spectra of the $Li_2O–Na_2O–B_2O_3$: MnO glasses recorded at room temperature in the wavelength range 300-700 nm are shown in Fig. 1. The absorption edge observed at 335 nm for glass L_0 is observed to shift towards slightly lower wavelength with increase in the concentration of Li_2O up to 40 mol %. For further increase in the concentration of Li_2O, the edge is observed to shift gradually towards lower wavelength. Additionally, due to the MnO doping, the spectrum of each glass exhibited one clear resolved absorption band between 375-650 nm. This band is assigned to transition $^6A_{1g}$ (S) $\rightarrow$ $^4A_{1g}$ (G)/^4E_g (G) of Mn^{2+} ions respectively [24-26]. With a gradual increase in the concentration of Li_2O in the range 0 to 40 mol %, the intensity of this band is observed to decrease. A summary of the data on the position of the corresponding band in the optical absorption spectra of $Li_2O–Na_2O–B_2O_3$: MnO glasses are presented in Table 2.

From the observed absorption edges, we have evaluated the optical band gaps (E_o) of these glasses by drawing Tauc plot between $(\alpha\hbar\omega)^{1/2}$ and ($\hbar\omega$) as per the equation:

$$(\alpha\hbar\omega) = C\,(\hbar\omega - E_o)^2. \qquad (1)$$

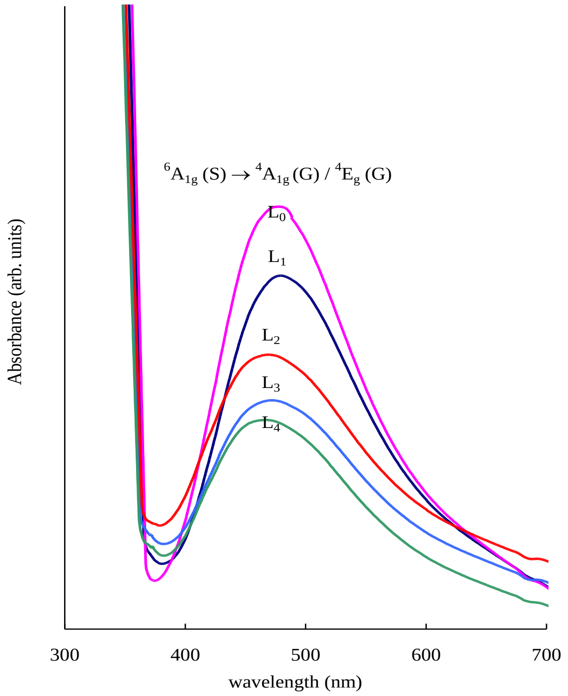

Fig. 1 Optical absorption spectra of $Li_2O–Na_2O–B_2O_3$ doped with MnO glasses

From an extrapolation of the linear portion of the curves of Fig. 2, the values of optical band gap (E_o) so determined are presented in Table 2. The value of the optical band gap is observed to be a maximum for the glass L_4.

Table 2: Summary of the data on optical absorption spectra of MnO doped $Li_2O–Na_2O–B_2O_3$ glasses

Glass	Cut-off wavelength (nm)	Band position (nm) $^6A_{1g}(S) \rightarrow {}^4A_{1g}(G) / {}^4E_g(G)$	Optical band gap (E_o)
L_0	335	477	3.62
L_1	331	473	3.63
L_2	328	470	3.64
L_3	325	467	3.67
L_4	323	465	3.70

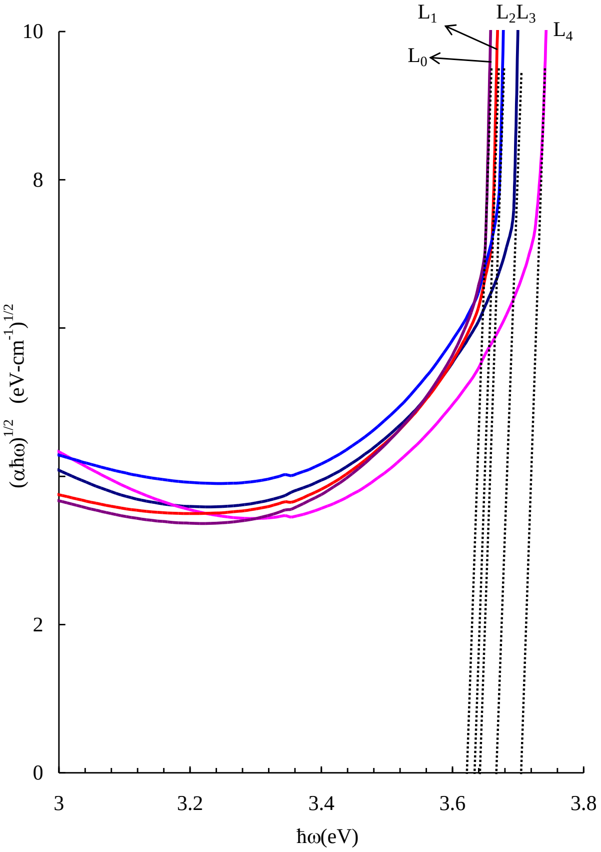

Fig. 2 Tauc pots of $Li_2O–Na_2O–B_2O_3$: MnO glasses

3.3 Infrared transmittance spectra

The infrared transmission spectra of $Li_2O–Na_2O–B_2O_3$: MnO doped glasses have exhibited two main groups of bands: (i) in the region 1200-1600 cm^{-1}, (ii) in the region 800-1200 cm^{-1} and another band at about 710 cm^{-1} (Fig. 3); these bands are identified due to the conventional stretching relaxation of B-O bond of the trigonal BO_3 units, vibrations of BO_4 structural units and due to the bending vibrations of B–O–B linkages respectively [27, 28].

When the concentration of lithium oxide increases, the intensity of the band due to BO_3 units is observed to decrease while the band due to BO_4 units is observed to increase. The summary of the data on various bands observed in the IR spectra of $Li_2O-Na_2O-B_2O_3$: MnO glasses is presented in Table 3.

Table 3: Summary of the data on various band positions (cm^{-1}) in IR spectra of $Li_2O–Na_2O–B_2O_3$: MnO glasses

Glass	BO_3 units	BO_4 units	B–O–B linkages
L_0	1399	1062	706
L_1	1402	1060	707
L_2	1408	1034	700
L_3	1411	1027	702
L_4	1414	1020	711

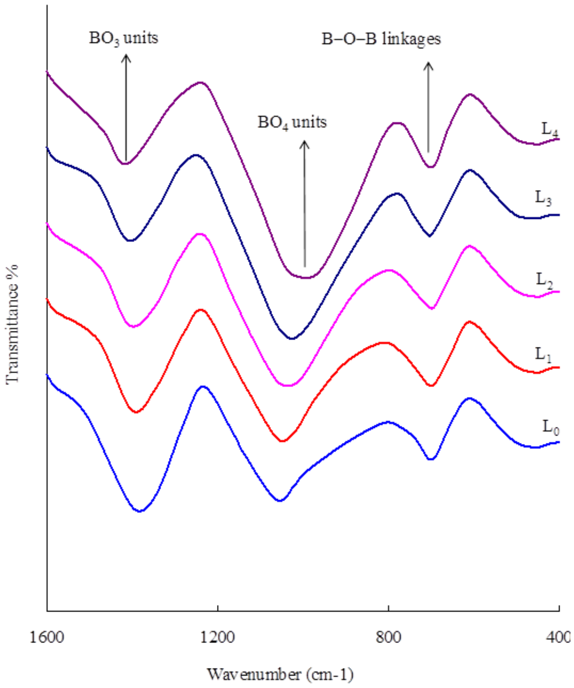

Fig. 3 IR spectra of Li_2O-Na_2O-B_2O_3 doped with MnO glasses

4. Discussion

$Li_2O–Na_2O–B_2O_3$: MnO glass network is an admixture of network formers, intermediate glass formers and modifiers. B_2O_3 is a strong network former and participate in the glass network with BO_3 and BO_4 structural units. The alkali oxides viz., Li_2O and Na_2O are the conventional modifiers, enter into the glass network by breaking B–O–B linkages; normally the oxygens of these oxides break the local symmetry while cations occupy interstitial positions.

It is well known that the spectroscopic properties of vitreous/crystalline materials depend on their structures. The structural borate units play a major role in deciding the nature of the physical properties in the glass matrices. Manganese ions in borate glasses might coexist in more than one valence state; mainly in Mn^{2+} and Mn^{3+}. These ions exist in different coordinations in glass matrices; for example, Mn^{3+} in both tetrahedral and octahedral and Mn^{2+} in octahedral environment depending on host glass composition and preparation conditions [29, 30].

In mixed alkali borate glasses, the optical absorption spectrum exhibits a single broad band centered at 470 nm (20,320 cm^{-1}). In a octahedral crystalline field of low to moderate strength, the five d electrons of Mn^{2+} ions are distributed in the t_{2g} and e_g orbitals, with three in the former and two in the later. 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 in the 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 broad band observed near ~ 20,320 cm^{-1} is assigned to ${}^6A_{1g}(S) \rightarrow {}^4A_{1g}(G)/{}^4E_g(G)$ transition of Mn^{2+} ions. As the concentration of Li_2O is increased there is a significant decrease in the intensity of this band is observed.

The validity of the quadratic relation (Eq. 1) related to optical band gap points out that the band gap is caused by amorphous optical absorption edge. This confirms the fact that the disordered amorphous glass materials are formed prevailingly by direct transitions between the valence band and the conduction bands and the absence of the indirect inter-band transitions like in the case of the crystals (i.e. the transitions in the different points of the Brillouin zone). Minor deviations observed from this dependence are understood due to trapping of some disordered states within the energy gap.

The value of optical band gap (E_o) decreases gradually with increasing Na_2O or decreasing Li_2O content in the glass network (Table 2). The alkali ions, depolymerize the glass network by creating more bonding defects and non-bridging oxygens (NBO). The increase in concentration of Na^{2+} ions (that have higher ionic radius when compared with that of Li^+ ions) in the glass network, an increase in the formation of donor centers is expected and subsequently, the excited states of localized electrons originally trapped on Mn^{2+} sites begin to overlap with the empty 3d states on the neighboring Mn^{3+} sites. As a result, the impurity or polaron band becomes more extended into the main band gap. This new polaronic development might have shifted the absorption edge to the lesser energy, which leads up to a significant decrement in the band gap as the concentration of Na_2O is increased.

The optical activation energy associated with the octahedral band of Mn^{2+} ions viz., ${}^6A_{1g}(S) \rightarrow {}^4A_{1g}(G)/{}^4E_g(G)$ is decreased from 2.67 eV to 2.59 eV with the increase in the concentration of Na_2O from 0 to 40 mol% or decrease in the concentration of Li_2O (Table 2); this is clearly a characteristic signal of inter valence transfer or a polaronic type of absorption. To be more specific, the associated electrons are trapped at shallow sites within the main band gap. In terms of polaronic perception, this kind of situation is only possible if the local potential fluctuation is small as compared to the transfer integral, j. A small overlap between electronic wave-functions (corresponding to adjacent sites) due to strong disorder is contributive to polaron formation. So in terms of the polaron exchange the variation of optical band gap can be explained as fallows: the electron delivered by the impurity atom at the Mn^{3+} site converts this into a lower valence state Mn^{2+} and at the next stage, the trapped electron at this Mn^{2+} site is transferred to the neighboring new Mn^{3+} site by absorbing a photon energy. Thus the optical absorption in the glass samples is dominated by polaronic transfer between the Mn^{2+} and Mn^{3+} species. The growth of this band with increase in the concentration of Na_2O (0 to 40 mol%) indicates the decrease in the oxidation of manganese ions from Mn^{2+} state to Mn^{3+} state.

The IR spectral studies also indicate a similar conclusion. As the concentration of Li_2O is increased (or Na_2O is decreased), the intensity of band due to BO_4 structural units is increased at the expense of BO_3 structural units. Such observation clearly suggests a decrease in the degree of disorder in the glass network with decrease in the concentration of Na_2O.

5. Conclusions

The optical absorption and IR spectra of Na_2O/Li_2O mixed alkali borate glasses doped with MnO have been carried out. The analysis of the results indicated that there is a decreasing proportion of manganese ions that oxidize from Mn^{2+} state to Mn^{3+} state as the concentration of Na_2O is increased from 0 to 40 mol%.

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