Effect Of Mn²⁺ On Physical And Spectroscopic Features Of Li₂B₄O₇ And K₂B₄O₇ Glasses With Teo₂

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Abstract

The present manuscript is to provide information about the preparation, and identification of the glassy nature, primary physical parameters, and structural studies of the effect of Mn^{2+} on $K_2B_4O_7$ -TeO_2 and $Li_2B_4O_7$-TeO_2 MnO[LTM] glasses. The glasses of thickness around 1 mm were obtained by the melt quenching method. These glasses are transparent enough to recognize them as glassy species but their amorphous nature was scientifically identified with peak-free XRD spectra. Several properties like density, molar volume, optical absorption, FTIR, Raman, and EPR spectra were measured and analysed, and discussed in detail. Density drastically decreased from 2.5176 gm/cc (LTM) to 2.3868 gm/cc (KTM) which is due to the presence of $K_2B_4O_7$. Molar volume increased from 66.27 (LTM) to 115.61 (KTM) glass sample. From Optical absorption spectra, optical band gap energy decreased from 3.278 eV (LTM) to 2.888 eV (KTM) and the refractive index increased. FTIR and Raman studies combined reveal the existence of certain structural groups and the domination of a few borate modes. EPR studies confirmed the presence of Mn^{2+} ions.

Keywords: Density, Molar volume, XRD, FTIR, Raman and EPR

I. Introduction

Oxide-borate glasses have unique properties like low glass forming temperature, very good thermal stability, wide spread of glass forming regions, and high devitrification towards TM ions, etc. have encouraged the researchers to probe these oxy-borate glasses. The introduction of TM ions into the glass matrix has opened a window that leads to several technological applications like optical windows, laser hosts, memory devices, Luminescent glasses, etc. [1,2]. Heavy metal oxides like Bi_2O_3 contribute to high-density glasses, if they are transparent they can be used in radiation shielding windows [3,4]. Heavy metal oxy-floro borate glasses the new promising materials that can be used in Radiation shielding applications due to their high densities, transparency, and low phonon energies, these can be used in active fibers [5]. There is a large scope to probe in this direction. Another aspect is the EPR studies which are very meagre on rare-earth fluoride doped glasses. EPR experimental technique will resolve the issue related to the oxidation state of the elements, their surrounding structure etc. There is an advantage in using $Li_2B_4O_7$ rather than using Li_2O and B_2O_3 as separate chemicals. Very few monograms were available on $Li_2B_4O_7$ in the literature [6,7]. $Li_2B_4O_7$ based glasses can find application in the preparation of solid-state batteries [8]. Tellurite based glasses have superior properties like high dielectric constant, high refractive index, large chemical stability, wide transmittance range of ~ 0.4 to 0.6 μm, broad homogeneity range, low melting point, low glass transition and non-hygroscopic nature. This makes them promising materials for photonic applications such as lasers, optical fiber amplifiers, non-linear optical devices applications and especially for electro-optic devices [9-12] .Manganese ions have been frequently used to modify the structure, The electric and magnetic properties of vitreous systems [13,14].Like other transition metal ions, manganese ions also exist in different valence states in glassy matrices.For example as Mn^{3+} in borate glasses with octahedral coordination whereas in silicate and Germinate glasses it exists in Mn^{2+} with both octahedral and tetrahedral coordination [15].

II. Experimental

The glass samples $80Li_2B_4O_7$-$19.5TeO_2$-$0.5MnO_2$ [LTM] and $80K_2B_4O_7$-$19.5TeO_2$-$0.5MnO_2$ [KTM] were processed by melt-quench process. The intrinsic chemicals are $Li_2B_4O_7$, $K_2B_4O_7$, TeO_2 and MnO_2 are Sigma-Aldrich with 99.9 % purity.For each glass composition, the required amounts of chemicalswere calculated based on mol% and weighed in electronic digital mono pan balance with an accuracy of ±0.001 mg. These

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ingredients were thoroughly grounded in a mortar with pestle to obtain homogeneous mixed powder. The mixture was placed in a platinum crucible and melted with the aid of an electrically heated carbide rod furnace at a temperature of 1050 ◦C. It took nearly half an hour for the mixture to melt congruently before it could be poured onto a hot stainless steel plate (100 ◦C) and pressed with another hot plate. The transparent glasses obtained are thermally relaxed at 100 ◦Cfor several hours to relieve stress.These transparent glasses are categorically tested for amorphous nature by peak free XRD spectra. The samples are tested on XRD Phillips Xpert pro diffractometer. Optical absorption transitions are noted in the range 300–900 nm on widely used Jasco 570 UV-VIS-NIR spectrometer with an ±0.1 nm accuracy operated at room temperature. Structural band vibrations are recorded in the range 400–1600 cm^{-1} on Perkin Emler Frontier FTIR with high resolution of 3 cm^{-1}. Molecular vibrations are documented in the range100–1500 cm^{-1} on the Jobin Yvon Horiba LABRAM-HR Raman spectrometer. The data is presented in this manuscript is carried out at room temperature.

At room temperature EPR spectra were scanned with 100 kHz modulating frequency and recorded between 50 mT and 450 mT at 9.6 GHz (X-band) on (JOEL FE-1X) EPR spectrometer.

Table 1 Composition of KLTC glasses, Band gap (Eg), Urbach energy (ΔE) and refractive index (n) values

Glass	K2B4O7 mol%	Li2B4O7 mol%	TeO2 mol%	MnO2 mol%	Eg(±0.001) ev	ΔE(±0.001) ev	n
LTM	0	80	19.5	0.5	3.278	0.2914	2.325
KTM	80	0	19.5	0.5	2.888	0.2770	2.427

III.   Results And Discussions

XRD spectra of KLTC glasses

The nature of the glass samples is verified with the primary experimental technic XRD. The amorphous nature of the samples is confirmed by the non-presence of sharp peaks in the spectra of XRD[16,17]. Figure.1 shows the combined XRD spectra of LTM and KTM glasses. The XRD spectra recorded for the angles between 10° to 80° clearly show no spikes in the spectra. The absence of sharp peaks in the spectra reveals the required amorphous nature of the LTM and KTM glasses.
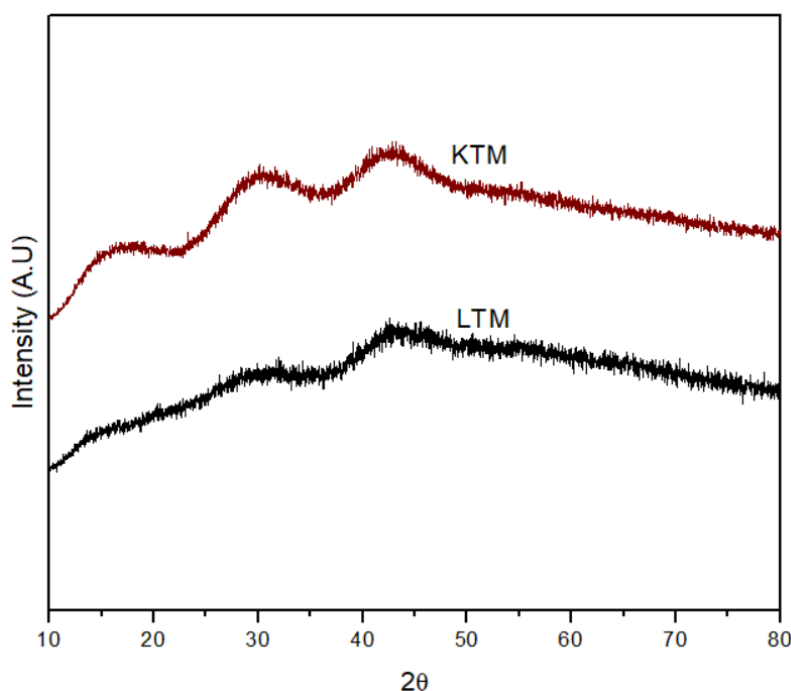

Fig. 1 XRD spectra of LTM and KTM glasses

Optical absorption spectra of LTM and KTM glasses

The absorption spectra of LTM and KTM glasses are shown in Figure.2 in which a distinct absorption edge can be seen in the vicinity of 400 nm. In addition, there is a wide absorption band located around 490 nm. The band is the typical absorption for the Mn^{2+} ions, and it is considered to be associated with the transition from $^2E_g \rightarrow ^2T_{2g}$ [18,19]. The smooth rise of the absorption edge around 400 nm is the result of the amorphous nature of the samples

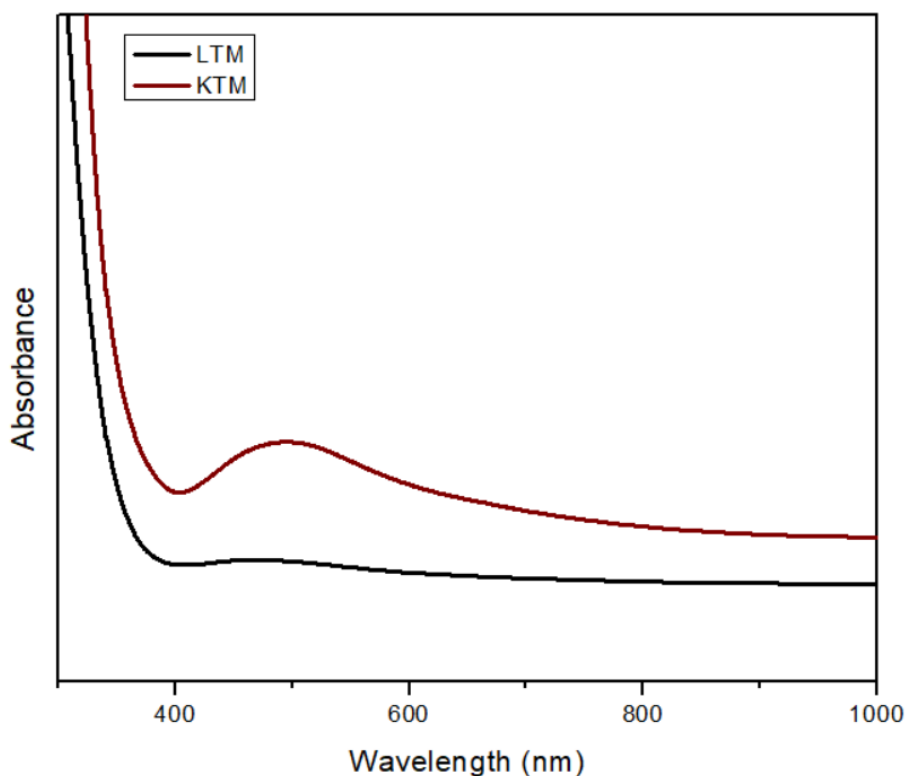**Figure.2. Absorption spectra of LTM and KTM glasses**

Figure 3. depicts the Tauc plot of glasses with the composition $80Li_2B_4O_7$-$19.5TeO_2$-$0.5MnO_2$ [LTM] and $80K_2B_4O_7$-$19.5TeO_2$-$0.5MnO_2$ [KTM] which were used to obtain the band gap energy (E_g) values. The optical band gap energy (E_g) is found by extending the linear portion of the $(\alpha h\upsilon)^{1/2}$ against $h\upsilon$ curve and determining where it meets the energy axis. The E_g values were reduced from 3.278eV (LTM) to 2.888eV(KTM).
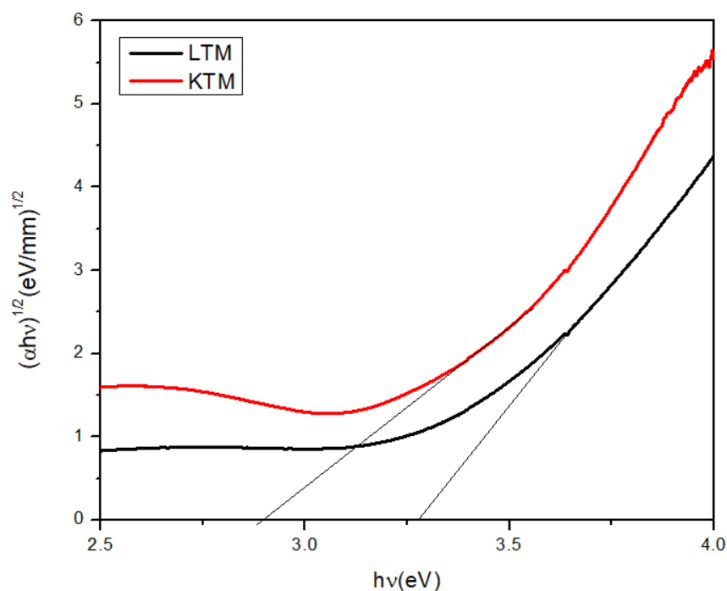
Figur 3. Tauc plot of LTM and KTM glasses

Figure 4. illustrates the Urbach plots of the LTM and KTM glasses, which may be used to determine the Urbach energy. These values may be derived by calculating the reciprocal of the slope obtained from the line drawn on the linear region of the curve. The Urbach energy of materials often characterizes the level of order in their structure. In this study, it was seen that ΔE for LTM is 0.2914 and for KTM is 0.2770 as the value of ΔE are so small that two samples are in good order.
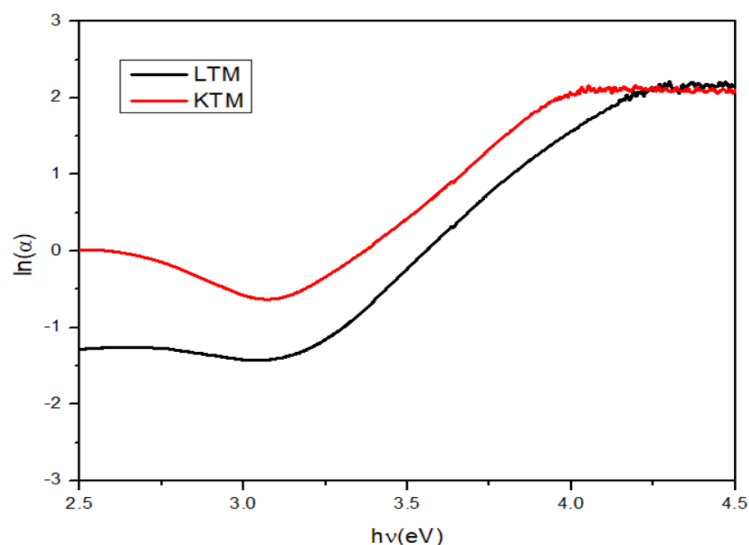
Figure 4. Urbach plot of LTM and KTM glasses,

EPR spectra of LTM and KTM glasses.

The Electron Paramagnetic Resonance (EPR) technique is used to study the local structure and environment of transition metal (TM) ions. The spin motion and orbital motion of an electron are the reasons for its acquisition of a magnetic dipole moment. The combined effects of electron orbital and spin angular momentum can be studied through EPR. Due to the minuscule energy of photons, we may disregard the magnitudes of molecular and electronic states, save for the ground state [20 - 23].

In the present work, the measured g-value is greater than the free electron g-value ($g_e = 2.0023$), indicating a negative shift (Δg). The negative shift in g-values of LTM and KTM glasses confirms that the Mn^{2+} ion are in an ionic environment. The ionic environment around the Mn^{2+} ions in LTM and KTM glass samples is almost the same, as the Δg remains largely the same. Both hyperfine splitting constant (A) and negative shift (Δg) confirm that in LTM and KTM glass samples are ionic in nature.

Figure.5 represents the EPR spectra of LTM and KTM glasses in which Mn^{2+} ions are added as paramagnetic probe to study the ligand filed around the Mn^{2+} ions
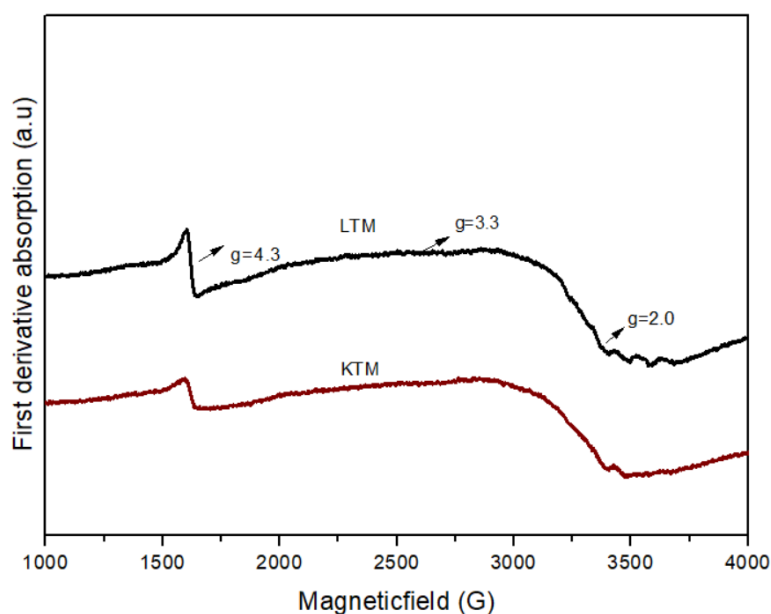

Figure.5. EPR spectra of LTM and KTM

The measured hyperfine (hf) splitting constant (A) for LTM is $107 \times 10^{-4} \, cm^{-1}$ and for KTM is $102 \times 10^{-4} \, cm^{-1}$. Based on these results it is concluded that the bonding between Mn^{2+} ions and its neighbouring ligands is ionic.

Table 2. spin – Hamiltonian parameters, hyperfine splitting constant of LTM and KTM glasses.

Glass code	g_l (low-field)	g_m (mid-field)	g_h (high-field)	$\Delta g = g_e - g_h$	$A(10^{-4}cm^{-1})$
LTM	4.3009	3.3080	2.0524	-0.0501	107
KTM	4.2906	3.3940	2.0829	-0.0806	102

FTIR and Raman Spectra of LTM and KTM glasses

The internal structure of the materials is explained through FTIR spectral analysis which is an extremely important factor. Fig. 6 demonstrates the FTIR spectra of LTM and KTM glasses. The spectra are recorded between the wavenumber 400 to 1600 cm^{-1}.

The IR bands related to various structural groups were registered in all the FTIR spectra. All the glass samples almost registered similar band positions with slight variations. The band positions as wavenumber (cm^{-1}) and their possible band assignments were recorded. The IR band 450-457cm^{-1} ascribed to Li^+ and K^+ metal cation vibrations. The non-linear variations of band intensities indicate mixed cation effect. The bands 700-758cm^{-1} are evolved due to stretching vibrations of boron-oxygen bonding along B-O-B axis. The wavenumbers 800cm^{-1} to 1000cm^{-1} are due to the stretching of B-O bonds in tetrahedral BO_4 units. Band around 1200cm^{-1} is due to the stretching vibrations of tetragonal BO_3 to BO_4 units. The bands in the wavenumber range 1300 to 1500cm^{-1} are due to the stretching vibrations of B-O linkage of BO_3 units [24,25,26].
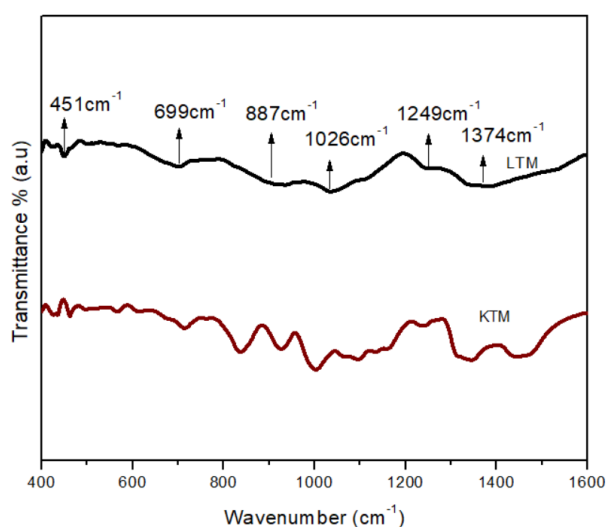

Figure 6. FTIR spectra of the LTM and KTM glasses

Raman spectra of LTM and KTM glasses are recorded at room temperature and scanned in the 400 to 1600 cm^{-1} wave number range. The Raman intensity in arbitrary units is taken on y-axis and scanned wave number is put on x-axis. Figure 4.10 shows the Raman spectra of LTM and KTM glasses.
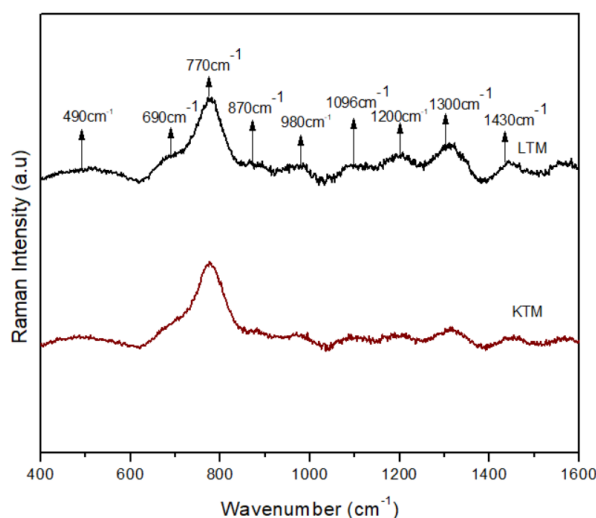

Figure 7. Raman spectra of the LTM and KTM glasses

Generally, broad band around 490 cm^{-1} is the result of symmetrically stretching vibrations of BO_4 units and it is also contributed by vibrations of Li-O and/or K-O bonds. A shoulder noticed around 690 cm^{-1} in both glass samples was believed to come from the vibrations B-O bands in six-membered borate rings with [BO_4] tetrahedral. 770 cm^{-1} is the most prominent peak in the entire spectra, and it arrived because of vibrations among B-O-B and B-O bond in the 6-membered borate rings [27]. The tetrahedral [BO_4] and Te-O band vibrations in TeO_4 units are also responsible [27]. In the vicinity of 980 cm^{-1} and 1096 cm^{-1} ortho, pyroborate groups dominate. The vibrations of BO_3 generated by the vibrations of stretching of B-O with NBO's are seen around 1190 to 1450 cm^{-1} [25,26].

IV.   Conclusions

The following conclusions have been drawn from the structural properties of $80Li_2B_4O_7$-$19.5TeO_2$-$0.5MnO_2$ [LTM] and $80K_2B_4O_7$-$19.5TeO_2$-$0.5MnO_2$ [KTM] glass using UV, EPR, FTIR and Raman Spectroscopy.

The presence of Mn^{2+} ions in these glasses is identified initially with brown colored glasses later the presence of Mn^{2+} ions is confirmed from the EPR spectra.

The absence of sharp peaks in the XRD spectra reveals the required amorphous nature of the LTM and KTM glasses

The band gap value for LTM is 3.278eV and for KTM is 2.888eV and is suggested that non-bridging oxygens are active in KTM glasses. Urbach energy values are small for both the glasses, ΔE for LTM is 0.2914 and for KTM is 0.2770

From EPR studies, The negative shift in g-values for both LTM and KTM glasses confirms that the Mn^{2+} ion are in an ionic environment. The measured hyperfine (hf) splitting constant (A) for LTM is 107x10^{-4} cm^{-1} and for KTM is 102x10^{-4} cm^{-1} also support the ionic character.

FTIR and Raman spectra revealed the occurrence of borate, tellurite, and metal cations groups and also confirmed the transformation of BO_3 to BO_4 units.

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