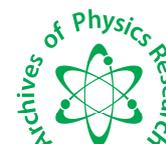




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Spectral Studies of Ba²⁺ and Mn²⁺ Ions Doped With Lithium Borate Glass At Room Temperature

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ABSTRACT

Thermo Gravimetric Analysis (TGA), Differential Thermal Analysis (DTA) and Fourier Transform Infrared spectroscopy (FTIR) measurements are performed on 20 Li₂O-(80-x) B₂O₃-xBaO and 20 Li₂O-(80-x) B₂O₃-xMnO glasses (where x = 0,10 to 20 in steps of 2 mol%) have been investigated to find out the role played by Ba²⁺ and Mn²⁺ on the structure of these glasses. The glass samples have been prepared using a conventional melt – quenching method. The glassy state of the sample is characterized using TGA and DTA measurements. The thermal stability of the glasses are increases with the doping of Ba²⁺ and Mn²⁺ in lithium borate glass. The FTIR data indicate the presence in the glasses of the BO₃, BO₄, Ba-O and Mn-O units and its dependence on the BaO and MnO content.

Keywords: TGA, DTA, FTIR and Thermal stability.

INTRODUCTION

Glasses are studied nowadays mainly because of the large applications that they span. B₂O₃ is one of the most common glass former and is present in almost all commercially important glasses [1]. Barium borate glasses are important because of their use as a non-volatile flux in the crystal growth of garnets and ferrites [2]. Borate glasses containing Li⁺ have been extensively studied due to their technological applications as solid electrolyte in electro chemical devices such as batteries [3].

DTA is a thermoanalytic technique, similar to differential scanning calorimetry. DTA curve provides data on the transformations that have occurred, such as glass transitions, crystallization, melting and sublimation. Glass transitions may occur as the temperature of an amorphous solid is increased. The ability to determine transition temperatures and enthalpies makes DTA a valuable tool in producing phase diagrams for various chemical systems. TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives and solvent residues. TGA and DTA have been applied to investigate the physical and chemical properties such as structure, crystalline transition, second order transition, fusion, vaporization, sublimation, absorption, adsorption, desorption, decomposition, oxidation, degradation and solid state reactions of the studied compounds [4]. An important use of DTA in glasses is to measure the glass transition temperature, T_g. For other glasses, however, crystallization or devitrification may occur at some temperature above T_g and below the melting point.

FTIR spectroscopy becomes effective tools for resolving the structure of local arrangement in glasses [5]. The infrared spectroscopy has been used since a long time to investigate the structure of different glasses [6]. This technique is most readily seen as contributing to the knowledge of structure and chemical bonding in various glasses [7]. IR spectroscopy is a very sensitive and one of the most used spectroscopy methods applied in the investigation of the local structure characterizing vitreous materials like oxide glasses [8]. Thus, the present work has been carried out to investigate the effect of barium and manganese ions doped with the lithium borate glasses with various spectroscopic techniques such as TGA, DTA and FTIR will give valuable information on these systems.

MATERIALS AND METHODS

The glass samples of the formula $20 \text{Li}_2\text{O}-(80-x) \text{B}_2\text{O}_3-x\text{BaO}$ (LBB) and $20\text{Li}_2\text{O}-(80-x) \text{B}_2\text{O}_3-x\text{MnO}$ (LBM) (where $x=0, 10$ to 20 in steps $2 \text{ mol } \%$) have been prepared by using the conventional melt-quenching technique. Required quantities of analytical grade of Li_2CO_3 , BaCO_3 , H_3BO_3 and MnCO_3 were obtained from E-merck, Germany and Sd-Fine chemicals, India. The proper compositions were mixed together by grinding the mixture repeatedly to obtain a fine powder. The mixture is melted in platinum crucible at about 1223 K and the same temperature was maintained for about 45 minutes to homogenize the melt. Then the glass samples were annealed at 573K for two hours to avoid the mechanical strains developed during the quenching process.

The glass transition (T_g), crystallization peak (T_p) and melting temperatures (T_m) were determined using differential thermal analysis (DTA) at heating rate of $20 \text{ }^\circ\text{C} / \text{min}$ in air using the instrument **SDT Q600 V8.3 Build 101**. The same instrument has been used for TGA measurement.

The thermal stability of glasses can be described by ΔT , which is defined as

$$\Delta T = T_p - T_g \quad \text{-----} \quad (1)$$

where ΔT gives the information about the devitrification tendency of the glasses. The difference between the glass transition temperature and the onset crystallization temperature, ΔT , has been commonly used as a rough criterion of the glass thermal stability against devitrification.

The FTIR transmission spectra of the glass samples were recorded at room temperature using KBr pellet technique with a Bruker Alpha – T FTIR spectrometer in the spectral range $500 - 3500 \text{ cm}^{-1}$. This powdered glass samples were thoroughly mixed with dry KBr in the ratio $1:20$ by weight and the pellets were formed using a pellet press. A SIC Glowbar source and a DTGS detector cooled with liquid nitrogen were used. For each spectrum 10 scans were made and the spectral resolution was 2 cm^{-1} .

RESULTS AND DISCUSSION

The TGA and DTA curves for the glasses (LB, LBB, LBM) prepared in this study are shown in the Figs. 1- 3. The TGA curves shows only small weight loss less than 3% in the complete range of investigation i.e. from 40 to 1000°C in all the glasses studied. These TGA and DTA thermograms of the present glasses also showed the amorphous nature of the glasses like XRD. The endothermic peaks corresponding to the glass transition (T_g) and exothermic peaks due to the crystallization (T_p) are clearly observed. It is, therefore, concluded that all melt - quenched samples prepared are glass. The values of glass transition temperature (T_g), crystallization temperature (T_p), melting temperature (T_m) and thermal stability ΔT estimated from DTA curves are summarized in Table 1.

Table 1 Values of glass transition temperature (T_g), crystallization peak temperature (T_p), melting temperature (T_m) and thermal stability (ΔT) of various glass samples.

Glass Samples label	Glass Composition in mol %	Glass transition temperature $T_g / ^\circ\text{C}$	Crystallization peak temperature $T_p / ^\circ\text{C}$	Melting temperature $T_m / ^\circ\text{C}$	Thermal stability $\Delta T / ^\circ\text{C}$
LB	20 – 80	288	617	834	329
LBB2	20 – 68 – 12	290	657	888	367
LBM2	20 – 68 – 12	295	671	878	376

It is seen that all the values of T_g , T_p and T_m increase with the doping of BaO and MnO content in lithium borate glass system. From the DTA scans, it is also observed that the lack of sharp endothermic and exothermic peaks evidently specify the formation of homogeneous glass. The change in the glass transition temperature T_g clearly shows that doping of BaO and MnO affects the glass structure. Specifically an increase in T_g with the addition of BaO and MnO contents indicates a increase in the rigidity of the glass network (Table 1). The analysis of these results indicates the increase in T_g with the addition of BaO and MnO content might be associated with the augmented cross-link density of various micro- structural groups and closeness of their packing [9]. Further, it has been known from the literature of the glasses that when a higher cross- link density of cation is replaced by a cation of lower cross- link density, T_g of respective glass should decrease [10, 11]. But in the present case this behavior was not observed. This could be due to the difference in cross-link densities of BaO and MnO. Therefore, the increase in T_g may be ascribed to the higher bond strength of Ba-O ($\approx 561.9 \text{ KJ mol}^{-1}$) and Mn-O ($\approx 402.9 \text{ KJ mol}^{-1}$) in comparison with the bond strengths of B-O ($\approx 192.7 \text{ KJ mol}^{-1}$) and Li-O ($\approx 150 \text{ KJ mol}^{-1}$) [12]. The T_g is also a measure of strength of the glasses [13].

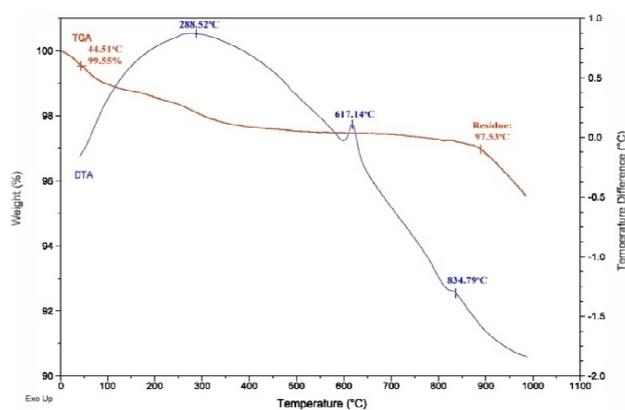


Fig 1: TGA and DTA curves for lithium borate glass (LB) at 20°C / min heating rate

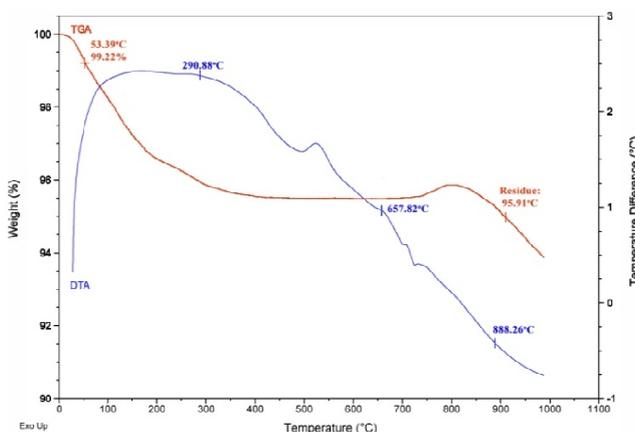


Fig 2: TGA and DTA curves for lithium borate barium glasses (LBB) at 20°C / min heating rate

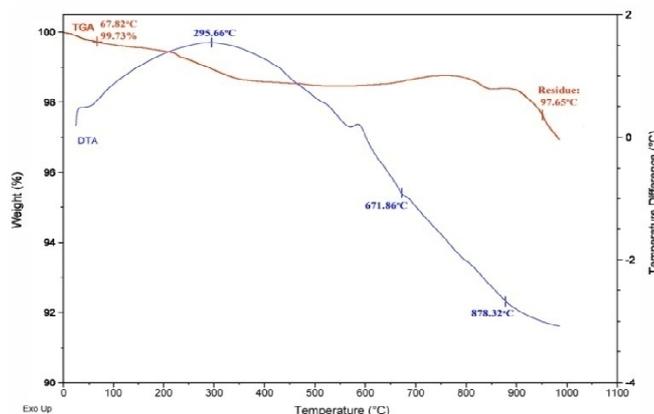


Fig. 3: TGA and DTA curves for lithium borate manganese glasses (LBM) at 20°C/min heating rate

Similarly, the observed increase in T_g , for glasses that are studied may be due to the decreasing number of non-bridging oxygen atoms (NBO) [14]. From this it may be concluded that the strength of the glasses increases with the doping of BaO and MnO contents. From the Table 1 it is also found that the thermal stability of glasses tends to increase with doping of BaO or MnO content. The increasing nature of ΔT suggests that the chemical bond strength of Ba-O and Mn-O bonds in the glasses is stronger than that of B-O bonds [15]. The thermal stability criterion ΔT of glasses is larger than 100° C, indicating that these glasses have good thermal stability and can easily be obtained in bulk forms [16].

The FTIR transmittance spectra of $\text{Li}_2\text{O-B}_2\text{O}_3$ (LB), $\text{Li}_2\text{O-B}_2\text{O}_3\text{-BaO}$ (LBB) and $\text{Li}_2\text{O-B}_2\text{O}_3\text{-MnO}$ (LBM) glasses were recorded over the range of 500 - 3500 cm^{-1} and are shown in Figs 4-6. The obtained transmission band and their assignments are summarized in Table 2.

A literature survey indicates that the vibrational modes of the borate network are mainly active in three infrared spectral regions. The regions are:

- (i) 600 - 800 cm^{-1} is due to bond bending vibration of B-O-B groups.
- (ii) 800 - 1200 cm^{-1} is due to the B-O stretching vibration of tetrahedral $[\text{BO}_4]$ units.
- (iii) 1200 - 1600 cm^{-1} is due to the asymmetric stretching of the B-O band of triangle $[\text{BO}_3]$ units [17-20].

In the studied glasses of LB, LBB and LBM, IR bands assignments have been summarized as follows.

(1) In pure B_2O_3 glass, the absorption peak at 806 cm^{-1} wavenumber is a characteristic band of boroxol ring. In the present glass systems the absence of this peak indicates non existence of boroxol ring formation, ultimately it consists of BO_3 and BO_4 groups [21, 22]. It is well known that the borate network consist of Sp^2 planar BO_3 units and more stable Sp^3 tetrahedral BO_4 units. Each BO_4 unit is linked with two such other units and one oxygen from each unit with a metal ion and the structure leads to the formation of long chain tetrahedrons. The presence of such BO_4 units is evident from the IR spectral studies. In general, BaO and MnO are a glass modifier and enters the glass network by breaking up the B-O-B bonds (normally the oxygen of BaO and MnO breaks the local symmetry while Ba^{2+} and Mn^{2+} ions occupy interstitial positions) and introduces coordinate defects known as dangling bonds along with non-bridging oxygen (NBO) ions. In this case, Mn^{2+} is octahedrally coordinated [23].

2) The band at Wavenumber $\leq 625 \text{ cm}^{-1}$ is due to the vibration of the modifier cations Ba^{2+} and Mn^{2+} . But these ions will act as glass modifier and convert the BO_3 triangles into BO_4 groups. Doping of these ions in the studied lithium borate glass seems to leads to the conversion in the direction of the NBO's formation [24, 25]. The band at $\sim 625 \text{ cm}^{-1}$ is due to specific vibration of Mn-O bonds. The existence of IR bands in the range 400 - 600 cm^{-1} indicates the presence of Ba-O and Mn-O tetrahedral bending vibration in the present glass system [26].

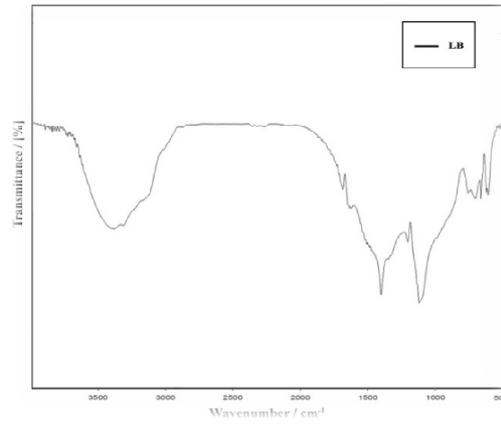


Fig.4 : FTIR spectra of $\text{Li}_2\text{O} - \text{B}_2\text{O}_3$ glass.

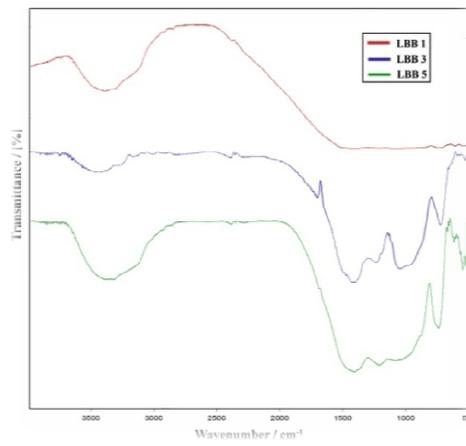


Fig.5: FTIR spectra of $\text{Li}_2\text{O} - \text{B}_2\text{O}_3$ glass with varying concentration of BaO.

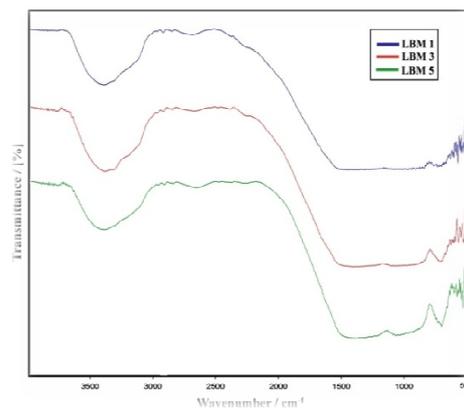


Fig. 6: FTIR spectra of $\text{Li}_2\text{O} - \text{B}_2\text{O}_3$ glass with varying concentration of MnO.

Table 2 Frequencies and their assignments for FTIR spectra of Ba²⁺ and Mn²⁺ ions in lithium borate glass at room temperature.

Glass samples label	Glass Composition in mol %	Wavenumber / (cm ⁻¹)	Assignments
LB	20 – 80	604 667 695 750 959 1116 1181 1334 144 1501 1598 1668 3397	600 - 750 cm ⁻¹ - Bending vibrations of B-O linkages 860 - 1200 cm ⁻¹ - B-O bond stretching of the tetrahedral BO ₄ units. 1200-1600 cm ⁻¹ -Asymmetric stretching vibrations of BO ₃ groups in ortho- and meta - borate units. ~3400 cm ⁻¹ - O-H group ≤ 62 cm ⁻¹ -Due to specific vibration of Ba-O and Mn-O bonds.
LBB1	20 – 70 –10	542 611 667 736 959 1042 1405 3393	
LBB3	20 – 66 – 14	528 570 611 715 945 1032 1181 1227 334 1417 1473 1697 3445	
LBB5	20 – 62 – 18	528 534 597 726 861 945 1098 1209 1399 3367	
LBM1	20 – 70 –10	625 736 875 975 1126 1195 1334 1440 3401	
LBM3	20 – 66 – 14	625 667 709 987 1126 1401 1251 3393	
LBM5	20 – 62 – 18	510 625 653 695 973 1126 1393 3401	

(3) The peak lying in 600 - 750 cm⁻¹ is assigned to the bending vibrations of B-O linkages in the borate network. The band around at 750 cm⁻¹ is assigned to the B-O-B bending vibration of bridges containing one trigonal and one tetrahedral boron [27].

(4) The second group of band is located in the region 860 - 1200 cm⁻¹ and originates from B-O bond stretching of the tetrahedral BO₄ units and is due to the vibration of some boron atoms attached to the non-bridging oxygen in the form of BO₄ vibration [28]. Further, these bands are assigned to B-O stretching vibration BO₄ units in tri, tetra and penta borate groups [29, 30]. The formation of band at 1126 cm⁻¹ which is present in the LBM glasses has been assigned to BO₄ stretching vibration [31, 32].

5) The peak lying in 1200 - 1600 cm⁻¹ is attributed to asymmetric stretching vibration of BO₃ groups in ortho- and meta-borate units [31]. The bands around at 1445 cm⁻¹ is due to B-O vibrations [33]. Further these bands are assigned to the meta borate chains [34]. i.e. formation of BO₄ on the expense of BO₃ with non bridging oxygen (NBO).

6) All the samples in the present systems show bands at about 3400 cm⁻¹ which is attributed to the O-H group [35].

CONCLUSION

The effect of Ba²⁺ and Mn²⁺ ions are doped with lithium borate glasses have been investigated using TGA, DTA and FTIR measurements. The glassy state of the sample is characterized using TGA and DTA measurements. Further, the increasing behaviour of T_g and ΔT indicates the increasing strength and thermal stability of the investigated

glass systems with doping of BaO and MnO content in lithium borate glass. In conclusion it has been found that MnO has more dominant effect than BaO in the glass network. The analysis of FTIR results suggests that the glass consists of BO₃, BO₄, Ba-O and Mn-O bridge bands forming a large glass network. It has also been observed that BaO and MnO contents help in converting BO₃ group to BO₄ units. This reveals that these ions also enter the glass structure as a network modifier. In the investigated glass system the four-fold boron atoms are dominated compared with the three-fold ones.

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