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COMPOSITION EFFECTS OF Al_2O_3 ON FTIR AND DTA IN LITHIUM BORATE GLASSES

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ABSTRACT

Lithium aluminum borate glasses of composition $35Li_2O$: (65-x) B_2O_3: xAl_2O_3 (where x = 0,5,10,15,20) were prepared by melting quenching technique and investigated by XRD, SEM, DTA and FTIR measurement. Differential Thermal Analysis showed that glass transition temperature changes due to change of composition. The FTIR analysis revealed that network structures of sample are mainly based on BO_3 and BO_4 unit.

KEYWORDS: Melt quenching, XRD, DTA and FTIR

INTRODUCTION

Chemical composition of glasses plays important role in determining the properties of the glasses. The glass is divided into main categories: network formers, network modifiers and intermediate species, which falls somewhere between network modifier and may be substituted for a network formed in the glassy state. Borate is one of the important glass former and has been incorporated into many kinds of glasses to attain desired chemical and physical properties. With borate glasses, B_2O_3 is the fundamental glass former because of higher bond strength, lower cation size, small heat of fusion and trivalent nature of in which B^{+3} ions are triangularly coordinate by oxygen and corner bonded in random configurations [1]. Borate glasses containing Li+ ions are considered to be a potential candidate for electrolytes of thin film batteries as the exhibit isotropic conductivity and stability at high voltage [2]. High vacancy cation such as Al^{+3} are commonly used as an intermediate species [3]. The structure of glasses with XB_2O_3 – (1-X) M_2O (M = Li, Na, K, Rb) consist B- O network, built up from planner three atoms $[BO_{3]}{}^{3-}$ and if an alkali oxide (M_2O) is added some of these unit transform into four coordinate tetrahedral [4]. Lithium borophosphate have been studied extensively in the literature [5-7] because of interesting structure and physical property changes upon network modification. The structural investigation of aluminum borate glasses has been studied by M. Kaur et al [8] and reported molar volume decreases with an increase in density of glass. The structural investigation has been studied in Li_2O:B_2O_3:Al_2O_3 glass system by using Al_2O_3 as mixed glass former [9]. The glass forming ability (GFA) and glass stability have been studied [10-14] on the basis of characteristic temperature measured by DTA and DSC.

In this work an attempt has been made for preparation and characterization of lithium borate glasses with the addition of Al_2O_3 as mixed farmer. The structural investigations of glasses have been studied with the help of XRD, FTIR spectroscopy, DTA and density measurement.

EXPERIMENTAL

The aluminum lithium borate glasses of composition $35Li_2O$: (65-X) B_2O_3: xAl_2O_3 (where X = 0,5,10,15,20) were prepared by melting quenching technique. The starting material, lithium carbonate, boric acid and aluminum oxide of AR grade purchased from Merc laboratory were used. A homogeneous mixture of different composition has melted in a ceramic crucible by keeping it into Muffle furnace equipped with digital temperature controller. The materials were melted at1150^{0}C for two hours with heating rate 30^{0}C/min and molted material is quenched in aluminum mould at room temperature (27^{0}C).The samples were annealed at 200^{0}C for 2Hrs in hot air oven. The measurements of XRD were carried out by using XPERT PRO DIFFRACTOMETER. The differential thermal analysis was measured by EFZ SCH STA 449F1 instrument in the temperature range 323K to 773K. FTIR of prepared samples was recorded by SHIMADZU FTIR spectrometer IR infinity1/8300 in the range 4000-400cm^{-1} with resolution 4 cm^{-1}. The density was measured by Archimedes principle.

RESULTS AND DISCUSSION

X- Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM)

The XRD spectra of investigating samples have been found as shown in Figure 1. X – Ray diffraction patterns recorded for all samples show a diffuse scattering over a range of angles (2θ from 10° to 100°), which confirms the amorphous nature of the samples.

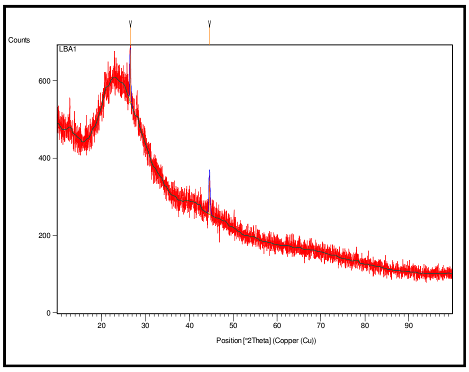

Figure 1: XRD of LB2A Sample

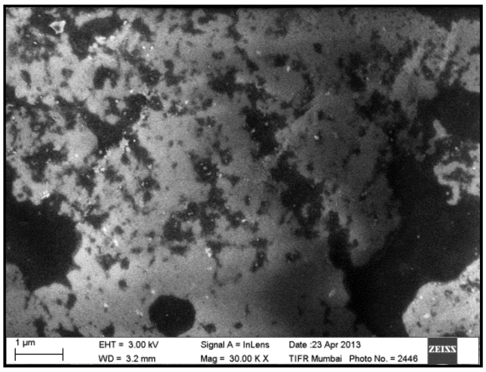

Figure 2: SEM of LB5A Sample

To study the surface morphology, scanning electron microscope results are obtained and are shown in Figure 2. It is clearly visible from the scan that the prepared glasses appear a homogeneous structure of glass flake suggesting a highly amorphous phase. The result of XRD and SEM shows that the prepared glasses are amorphous in nature.

Fourier Transform Infrared Radiation (FTIR)

The results have been discussed on the basis of the method given by Condrate and Tarte [15-16] by comparing experimental data of the glasses with those of related crystalline compounds. The characteristic curve for B_2O_3, Li_2O and Al_2O_3 were used as a reference point in the discussion. The structural analysis of oxide glasses is carried out by using following information [17-18].

- Type of the bridged bonds of oxygen, which link the co-ordination polyhedral of the framework and composition of chemical inhomogeneities in the structure of the glass.
- The coordination number of the compound with respect to oxygen, especially on the former network.
- The change in oxygen bonds of framework induced by cation modifiers which combine with the oxygen bonds.

The FTIR absorption spectra of investigating samples for the region 400-4000 cm^{-1} are shown in Figure 3. The IR spectra of these investigated samples show the number of sharp, medium and broad absorption peaks. Due to close and overlapping bands, obtained spectra appear more complex. The vibrational modes of borate network are mainly active in three infrared spectral region, which are similar to those reported by several workers [15-19]**.** First band occurrence at 1200-1600cm^{-1} is due to asymmetric stretching, relaxation of a B-O band of trigonal BO_3 unit. Second band between 800cm^{-1} and 1200cm^{-1} is due to B-O bond stretching of the tetrahedral BO_4 unit and third group observed around 700cm^{-1} is due to bending of B-O-B linkage in the borate network**.**

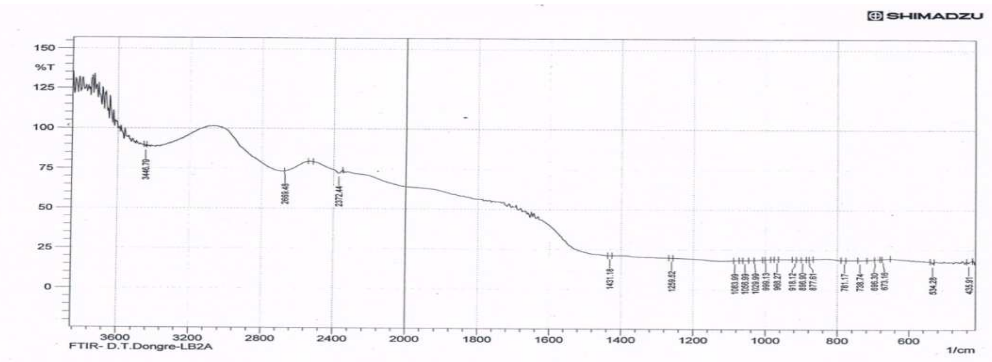

Figure 3: FTIR of LB2A Sample

The FTIR absorption bands obtained from this series (LB1A-LB5A) are at 422 cm^{-1}-486cm^{-1}due to the presence of lithium oxide in the samples. The bands situated in the range 501cm^{-1}-574cm^{-1} is assigned by B-O-B bands bending vibrations of various borate segments and next one is at 700cm^{-1}-794 cm^{-1} is attributed to the deformation and bending vibrations B-O-B linkage in borate network. It has been observed that LB3A and LB4A samples show maximum absorption and shift toward lower wave number. The maximum bands appear in these samples (LB3A and LB4A) in the range 800cm^{-1}-1200cm^{-1} are due to stretching of the tetrahedral BO_4 unit**.** In the region 1200-1600cm^{-1}, bands appear in the range 1236cm^{-1}-1477cm^{-1} due to B-O bond of trigonal BO_3 unit. The band that appears above 1500 cm^{-1} can be assigned to presence water group and O-H vibration.

Differential Thermal Analysis (TG-DTA)

The TG –DTA curves of the sample is shown in Figure 3. The TG profile of the LB1A sample shows that weight loss is taking place in the three step process in the temperature range 300K-770K. The initial weight loss takes place between 300K-443K due to decomposition of organic compound that were added while grinding raw chemicals to obtain homogeneity and water present in the sample which is about 1.7 %. A weight loss of 2% has been noticed in the temperature range 444K-650K due to phase change of H_3BO_3 to B_2O_3.Final weight loss 0.1% have been observed in the temperature range 651K-720K, that could be a decomposition of Li_2CO_3 to Li_2O and thereafter no appreciable weight loss has been noticed in the sample due to the formation of stable compound. In all samples, the DTA profile shows an endothermic peak at 350K which is due to partial melting of small percentage of impurity and phase change of H_3BO_3 to B_2O_3.The glass transition temperature has been noticed at 478K.

The TG profile of the sample LB2A shows that the weight loss is taking place in the three steps in the range 300K-760K.The initial weight loss takes place between 300K-443K due to decomposition of organic compound that were added while grinding raw chemicals and water present in the sample which is about 0.8%. The weight loss of 1.2% has been noticed in the range of 444K-650K due to phase change of H_3BO_3 to B_2O_3. Final weight of 0.15% has been observed in the temperature range of 651K-720K, that could be a decomposition of Li_2CO_3 to Li_2O and thereafter no appreciable weight loss has been identified in the sample due to the formation of stable compound. The glass transition temperature has been observed at 522K.

The TG profile of LB3A sample, initial weight loss of 0.2% has been observed in the temperature range 300K-443K due to decomposition of the raw materials and water. The weight loss of 0.1% has been observed in the temperature range 444K-650K, that could be due to phase change of H_3BO_3 to B_2O. Final weight loss of 0.05% has been identified due to decomposition of Li_2CO_3 to Li_2O in the range of 651K-720K and thereafter no weight loss has been observed due to the formation of stable compound. The glass transition temperature has been noticed at 620K.

In the TG curve of the sample LB4A, initial weight loss of 0.1% has been identified in the temperature range 300K-443K due to decomposition of raw material and water. The weight loss of 0.2% has been observed in the temperature range of 444K-650K due to phase change of H_3BO_3 to B_2O_3 and thereafter no appreciable weight has been noticed in the sample due to the formation of stable compound. The glass transition temperature has been noticed at 720K.

In TG profile of LB5A sample, initial weight loss takes place between the temperature range 300K-443K due to decomposition of raw material and water, which is about 0.3%. The weight loss of 0.4% has been observed in the temperature range of 444K-650K due to phase change of H_3BO_3 to B_2O. Final weight loss of 0.3% has been identified due to decomposition of Li_2CO_3 to Li_2O in the range of 651K-720K and thereafter no noticeable change has been observed due to the formation of stable compound. The glass transition temperature has been observed at 585K.The higher glass transition temperature has been observed for LB4A sample.

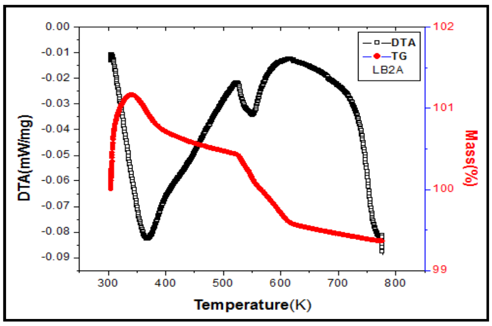

Figure 4: TG-DTA of LB2A sample

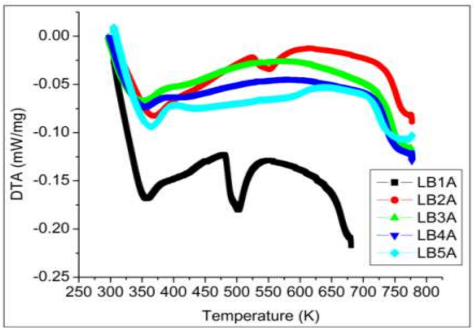

Figure 5: DTA of Sample LB1A-LB5A Sample

It has been revealed that as a percentage of Al_2O_3 increase, weight loss reduces and stability of compound increases. The reduction of weight loss with variation of glass temperature has been observed due to structural changes in the glasses.

The DTA curves of investigating samples (LB1A-LB5A) are shown in Figure 5. The values of glass transition temperature (Tg), onset melting point temperature (TX) and offset melting point temperature (T_1) obtained from graph are depicted in the Table 1. The effect of the percentage of Al_2O_3 and the former ratio of thermal transition data for these investigated samples is shown in table 1. In the series LB1A-LB5A, it has been observed that the glass transition temperature shifted to higher temperature with increase Al_2O_3 content up to 15 mole percent Al_2O_3 in glass sample and then shifted to lower temperature. The highest value of T_g is found for 15 mole percent of Al_2O_3. The substitution of former Al_2O_3 in Li_2O:B_2O_3 causes change in the value of T_g. The increase in T_g value reveals that the structure of the glass sample is modified. Glass reduced temperature (T_{rg}) has higher value at 15 mole percent of Al_2O_3 content glass sample, indicate GFA and high thermal stability. The value of γ is higher for 15 mole percent of Al_2O_3 sample in series LB1A-LB5A. It shows that this sample has higher thermal stability. The comparative value of ΔT_x is high for this sample. It reveals that this sample is not a fully glassy state and not the crystalline state. The value of K_H is high for LB4A glass sample indicates greater stability of glass against devitrification. The glass sample (LB3A) has a lower value of $\Delta T_{x.}$ This indicates that super cooled liquid cannot exist in wide range without crystallization and it has low resistance to the nucleation and growth of crystallization phases.

Table 1: The Values Obtained from TG DTA Graph of LB1A-LB5A Samples

Sample	Mole % Al_2O_3	Tg	Tx	Tp	T1	Trg	ΔTx	γ	K_H
LB1A	0	478	502	542	650	0.73	24	0.445	0.135
LB2A	5	522	555	625	760	0.68	33	0.432	0.138
LB3A	10	620	630	720	762	0.81	10	0.455	0.075
LB4A	15	720	755	770	767	0.95	35	0.499	0.744
LB5A	20	585	630	650	770	0.76	45	0.464	0.243

CONCLUSIONS

According to the results obtained, it can be concluded that investigated glass samples are composed of glassy phase. The increase in mole percent of Al_2O_3 changes the structure of the sample from partial crystalline phase to fully glassy phase. The results of SEM are same as that of XRD results. From FTIR results, it is concluded that Al_2O_3 enters in the glass network as modifier and former. The BO_3 and BO_4 act as a network structural group while lithium and aluminum appear in interstitial positions. Formation of BO_3 and BO_4 units to increase in mole percent of Li_2O and Al_2O_3 is also confirmed by FTIR spectroscopic studies. The glass transition analysis, mass loss of the sample decreases with increase in mole percent of Al_2O_3. The GFA parameters ΔTx and γ follow the same trends with GS parameter K_H. The glass sample LB4A was higher thermal stability against crystallization. The density of glass increases and molar volume decreases with increase in mole percent of aluminum oxide.

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