Evaluation of Glass Forming Tendency
of Lithium Borate Glass by DTA

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ABSTRACT

The ionic conducting glasses of modifier ratio η = 1.8571 and former ratio y = (0.69≤ y ≤ 1) have been prepared with various composition by using melt quenching technique and investigated by XRD,SEM, and DTA measurement. XRD and SEM confirmed the nature of glasses. The reduced glass transition temperature (T_{rg}), width of the super cooled liquid (ΔT_x), reduced crystallization temperature (γ) and Hurby parameter (K_H) was determined from TG-DTA graph. Differential Thermal Analysis showed that glass transition temperature changes due to change of composition. The thermal analysis revealed that mass loss of sample decreases with increase in mole percent of Al_2O_3 and the GFA parameters ΔTx and γ follow the same trends with GS parameter K_H. The glass sample content of 15 mole percent of Al_2O_3 was higher thermal stability against crystallization.

Keyword*: *DTA, GFA, Melt quenching, SEM, XRD.

I. INTRODUCTION

Chemical composition of glasses play important role in determining 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 former in the glassy state. Glasses are more advantages than crystalline material because of their structural properties, absence of grain boundaries and variation due to composition [1].Borate glasses have been investigated due to its open like structure. Addition of modifier of modifier Li_2O borate glass composition changes the structure and transforms BO_3 triangles to tetrahedral along with thermal stability [2-3]. Glass transition temperature, being itself a useful parameter in glass technology, is sensitive to structural changes, which can occur due to compositional changes [4–6]. The glass-forming ability (GFA) of a melt is evaluated in terms of the critical cooling rate for glass formation, which is the minimum cooling rate (Rc) necessary to keep the melt amorphous without precipitation of any crystals during solidification. The smaller Rc, the higher the GFA of a system should be. However, Rc is a parameter that is difficult to measure precisely. A great deal of effort has therefore been devoted to search for a simple and reliable gauge for quantifying GFA for the melt. As result, many criteria have been proposed to reflect relative GFA on the basis of the characteristic temperatures measured by differential scanning calorimeter (DSC) or/and differential thermal analysis (DTA) [7–14]. The endothermic peak corresponds to the glass transition while the exothermic peak indicates the crystallization point of the glass. The glass transition (Tg) as well as crystallization temperatures (Tc) are estimated by the slope intercept method. The nature of the DSC curves is typical for other glass compositions. Thermal study of the glasses were performed because any change in the coordination number of network forming atoms, or the formation of non bridging oxygen, is

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known to be reflected in the Tg. DSC study reveals that both Tg and Tc increase monotonically with the increase of B_2O_3 content, which is the network former here. It is reported that generally Tg and Tc in-creases with the increase of network former/glass former [15] which is observed in this present study also. How-ever several reports of germinate anomaly are there which shows a decrease in Tg with the increase of GeO_2 content in the glass system [16]. It is believed that Tg is depend on the strength of chemical bonds in the structure and maximum value of T_g is reported in the B_2O_3 content glasses [17-18]. The structural investigation have been studied with DTA in $Li_2O:B_2O_3:Al_2O_3$ glass system by using Al_2O_3 as mixed glass former [19]. The glass forming ability (GFA) and glass stability have been studied [20-21] on the basis of characteristic temperature measured by DTA and DSC. In this work an attempt has been made for preparation and investigation of thermal analysis of lithium borate glasses with addition of Al_2O_3 as mixed former.

II. MATERIAL PREPARATION AND 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 melt 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 ceramic crucible by keeping it into Muffle furnace equipped with digital temperature controller. The materials were melted at 1150^0C for two hours with heating rate 30^0C/min and molted material is quenched in aluminum mould at room temperature (27^0C). The samples were annealed at 200^0C for 2Hrs in hot air oven.

The glasses are prepared by changing former ratio with constant modifier ratio.

Modifier Ratio $\eta = \dfrac{B_2O_3 + Al_2O_3}{Li_2O}$ **Former Ratio** $y = \dfrac{B_2O_3}{B_2O_3 + Al_2O_3}$

The measurements of XRD were carried out by using XPERT PRO DIFFRACTOMETER. It confirms the nature of glasses. The differential thermal analysis was measured by EFZ SCH STA 449F1 instrument in the temperature range 323K to 773K. The values of glass transition temperature (Tg), onset melting point temperature (Tx) and offset melting point temperature (T_1) obtained from TG-DTA graph. The GFA parameters ΔTx, γ and K_H were calculated by using following relations.

Reduced glass transition temperature Trg = Tg /T1 ……………………………………(1)

$$\Delta Tx = Tx - Tg \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Reduced crystallization temperature γ = Tx /Tg+T1 ……………………………… (3)

Hurby Parameter KH = (Tx-Tg) /(T1-Tx) ....(4)

III. RESULTS AND DISCUSSION

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

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

To study the surface morphology, scanning electron microscope results are obtained and are shown in Fig.2. It is clearly visible in SEM that the prepared glasses appear a homogeneous structure of glass flake suggesting highly amorphous phase. The result of XRD and SEM shows that the prepared glasses are amorphous in nature.
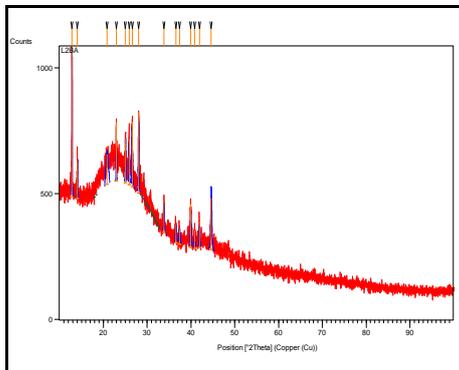
Fig.1: XRD of LB3A sample
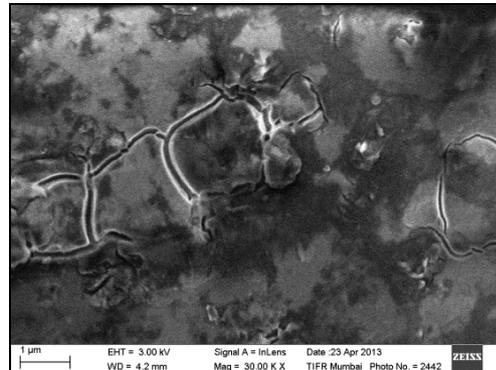
Fig.2: SEM of LB3A sample

3.2 Differential Thermal Analysis (TG-DTA)

The TG –DTA curves of the sample is shown in Fig.3. The TG profile of the LB1A sample shows that weight loss is taking place in the three steps 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% has been observed in the temperature range 651K-720K, that could be decomposition of Li_2CO_3 to Li_2O and thereafter no appreciable weight loss has been noticed in the sample due to formation of stable compound. In all samples, the DTA profile shows 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 decomposition of Li_2CO_3 to Li_2O and thereafter no appreciable weight loss has been identified in the sample due to 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 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 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 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 formation of stable compound. The glass transition temperature has been observed at 585K.The highest glass transition temperature has been observed for LB4A sample.

It has been revealed that as percentage of Al_2O_3 increases, 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 investigated samples (LB1A-LB5A) are shown in Fig 3. The values of glass transition temperature (Tg), onset melting point temperature (Tx) and offset melting point temperature (T_1) obtained from graph and the effect of percentage of Al_2O_3 on thermal transition data for these investigated sample is depicted in Table 1. In the series LB1A-LB5A, it has been observed that 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 fully glassy state and not 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 lower value of ΔT_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.

(a)

(b)

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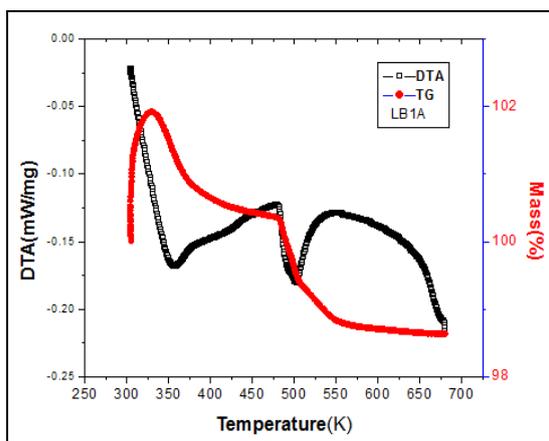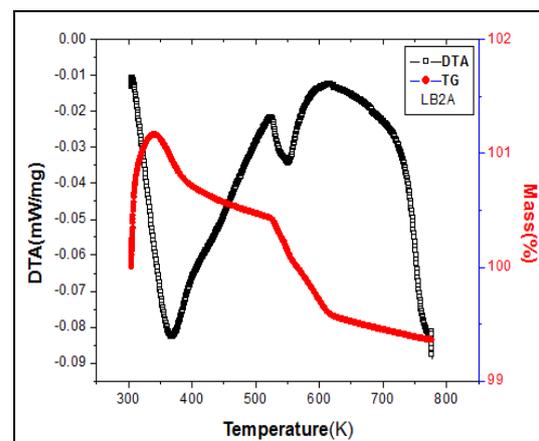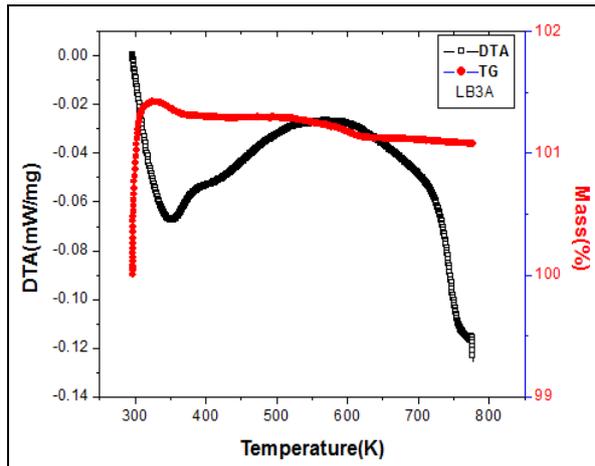
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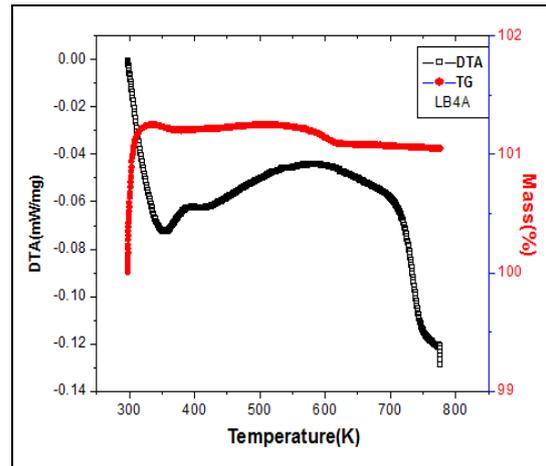
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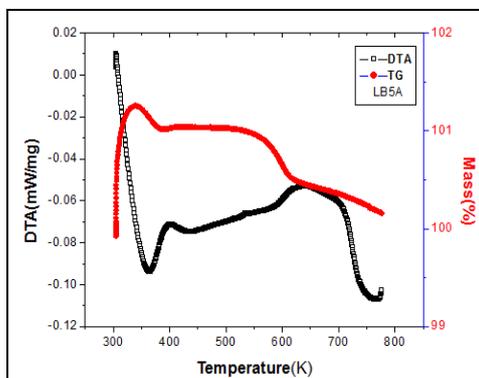
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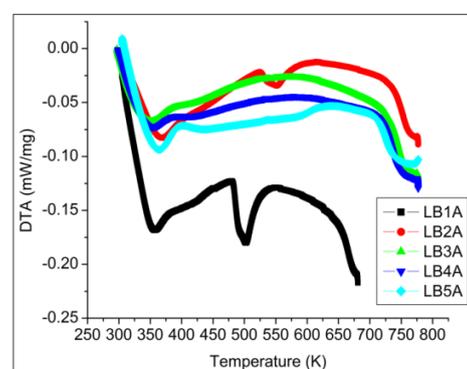
(f)

Fig.3:TG-DTA curves of sample (a) LB1A (b) LB2A (c) LB3A (d)

LB4A (e) LB5A (f) DTA curve of LB1A-LB5A samples.

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

IV. CONCLUSION

According to the results obtained, it can be concluded that investigated glass samples are composed of glassy phase. The glass transition analysis shows that mass loss of 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 of 15 mole percent of Al_2O_3 was higher thermal stability against crystallization.

V. AKNOLEDGEMENT

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