



Thermal Stability and Glass Forming Ability of Li^+ Ion Conducting Glasses

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ABSTRACT

The ionic conducting glasses of modifier ratio $\eta = 1.5$ and former ratio $y = 0.66 \leq y \leq 1$ have been prepared with various composition by using melt quenching technique. The nature of glass samples were confirmed by XRD and SEM. 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 ΔT_x and γ follow the same trends with GS parameter K_H . The glass sample content of 5 mole percent of Al_2O_3 was higher thermal stability against crystallization.

Keywords: Melt quenching, XRD, SEM, DTA and GFA

I. INTRODUCTION

Thermal analysis is the analysis of a change in property of a sample, which is related to an imposed change in temperature. Thermo Gravimetric Analysis (TG) is more useful for dehydration, decomposition, desorption, and oxidation process. 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 (R_c) necessary to keep the melt amorphous without precipitation of any crystals during solidification. The smaller R_c , the higher the GFA of a system should be. However, R_c 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 (T_g) as well as crystallization temperatures (T_c) 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 known to be reflected in the T_g . DSC study reveals that both T_g and T_c increase monotonically with the increase of B_2O_3 content, which is the network former here. It is

reported that generally T_g and T_c increases with the increase of network former/glass former [15-18] which is observed in this present study also. The glass forming ability (GFA) and glass stability have been studied [19-20] on the basis of characteristic temperature measured by DTA and DSC.

In this work an attempt has been made to study the investigation of thermal stability and glass forming ability of Li^+ ion conducting glasses with addition of Al_2O_3 as mixed former.

II. MATERIAL PREPARATION AND EXPERIMENTAL

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°C for two hours with heating rate $30^\circ\text{C}/\text{min}$ and molted material is quenched in aluminum mould at room temperature (27°C). The samples were annealed at 200°C for 2Hrs in hot air oven.

$$\text{Modifier Ratio } (\eta) = \frac{\text{B}_2\text{O}_3 + \text{Al}_2\text{O}_3}{\text{Li}_2\text{O}}$$

$$\text{Former ratio } (y) = \frac{\text{B}_2\text{O}_3}{\text{B}_2\text{O}_3 + \text{Al}_2\text{O}_3}$$

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 (T_g), onset melting point temperature (T_x) and offset melting point temperature (T_1) obtained from TG-DTA graph. The GFA parameters ΔT_x , γ and K_H were calculated by using following relations.

Reduced glass transition temperature

$$T_{rg} = T_g / T_1 \quad \dots\dots\dots(1)$$

$$\Delta T_x = T_x - T_g \quad \dots\dots\dots(2)$$

Reduced crystallization temperature

$$\gamma = T_x / T_g + T_1 \quad \dots\dots\dots(3)$$

Hurby Parameter

$$K_H = (T_x - T_g) / (T_1 - T_x) \quad \dots\dots\dots(4)$$

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

The XRD spectra of investigated samples have been found as shown in Figure 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 Figure 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.

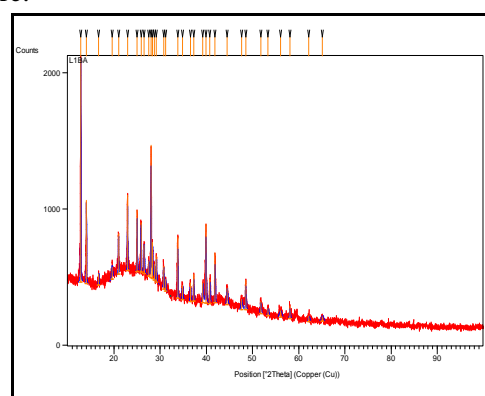


Figure 1. XRD of LBA1 sample

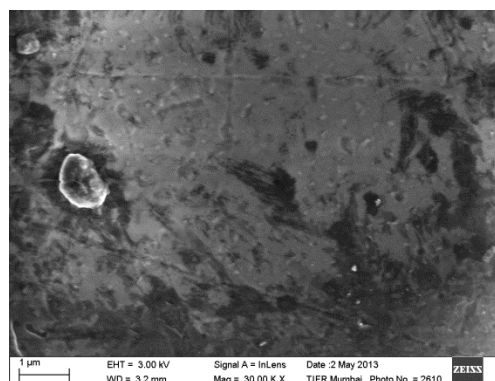
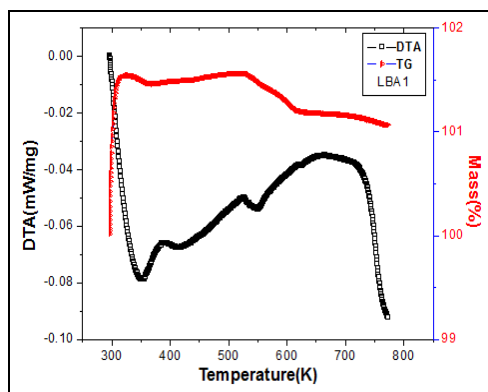


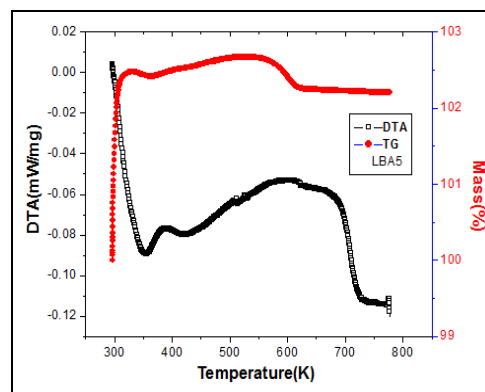
Figure 2. SEM of LBA5 sample

Thermal analysis (TG-DTA) of glass samples

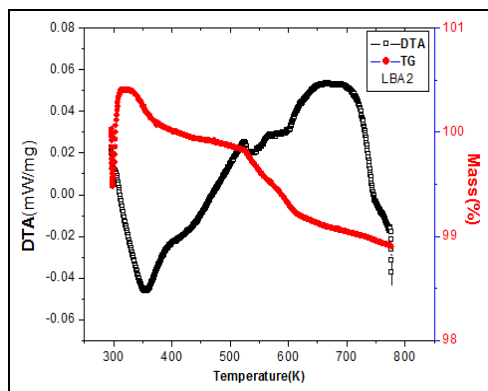
The TG –DTA curves of the LBA1-LBA5 samples are shown in the Figure 3. The TG profile of the LBA1 sample shows that weight loss is taking place in the multi steps process in the temperature range 300K-760K. The initial weight loss takes place between 300K-443K due to decomposition of organic compound that were added while grinding raw chemicals to obtain homogeneity and water present in the sample



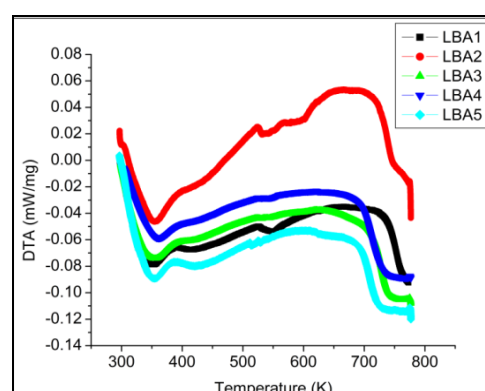
(a)



(e)

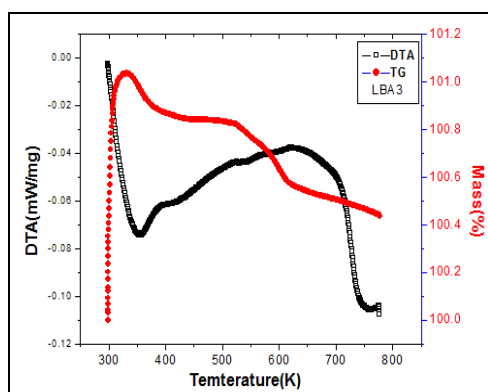


(b)

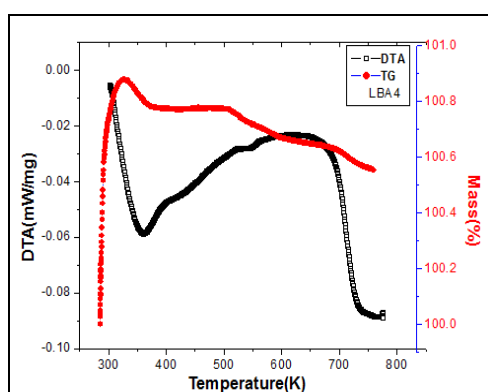


(f)

Figure 3. TG-DTA curves of samples (a) LBA1 (b) LBA2 (c) LBA3 (d) LBA4 (e) LBA5 (f) DTA curve of samples LBA1- LBA5



(c)



(d)

which is about 0.15%. A weight loss of 0.5% has been noticed in the temperature range 444K-650K due to phase change of H_3BO_3 to B_2O_3 . Final weight loss of 0.1% has been identified 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 attributed 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 520K.

The TG profile of the sample LBA2 shows that the weight loss is taking place in the three step 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 0.6%. The weight loss of 0.8% has been noticed in the range of 444K-650K due phase change of H_3BO_3 to B_2O_3 . Final weight loss of 0.2% has been observed in the temperature range

of 651K-720K, that could be due to 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 noticed at 527K.

The TG profile of LBA3 sample, initial weight loss of 0.3% has been observed in the temperature range 300K-443K due to decomposition of the raw materials and water. The weight loss of 0.3% has been observed in the temperature range 444K-650K, that could be decomposition of Li_2CO_3 to Li_2O and final weight loss of 0.1% has been identified in the range of 651K-770K and thereafter no weight loss has been observed due to formation of stable compound. The glass transition temperature has been observed at 524K.

In the TG curve of the sample LBA4, initial weight loss of 0.1% has been identified in the temperature range 300K-443K due to decomposition of raw materials and water. The weight loss of 0.1% has been observed in the temperature range of 444K-650K due to phase change of H_3BO_3 to B_2O_3 . Above 651K no appreciable weight loss has been noticed in the sample due to formation of stable compound. The glass transition temperature has been found to be 530K.

In TG profile of LBA5 sample, initial weight loss of 0.05% takes place between temperature range 300K-443K due to decomposition of raw materials and weight loss of 0.5% has been observed in the temperature range 444K-650K. Above temperature 651K no noticeable change has been observed due to formation of stable compound.

It reveals that weight loss reduces and stability of compound increases with increase in percentage of Al_2O_3 . It reflects that the structure of glass is changed due to mixed former effect.

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