Thermal Analysis of Li2O-B2O3-AL2O3 Glass System

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Abstract—Lithium aluminum borate glasses of composition 35Li2O : (65-x) B2O3 : xAl2O3 (where x = 0, 5, 10, 15, 20) were prepared by melt quenching technique and investigated by XRD, SEM, and DTA measurement. XRD and SEM confirmed the nature of glasses. 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 Al2O3, and the GFA parameters \( \Delta T_c \) and \( \gamma \) follow the same trends with GS parameter \( K_{GS} \). The glass sample content of 15 mole percent of Al2O3 was higher thermal stability against crystallization.

Index Terms—DTA and 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. Borate is one of the important glass former and has been incorporated in many kind of glasses to attain desired chemical and physical properties. In borate glasses, B2O3 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 configuration [1]. Borate glasses containing Li\(^+\) ions are considered to be potential candidate for electrolytes of thin film batteries as the exhibit isotropic conductivity and stability at high voltage [2]. High vacancy cation such as \( A^{1+3} \) are commonly used as intermediate species [3]. The structure of glasses with \(XB_2O_3 \cdot (1-X)M_2O\) (M = Li, Na, K, Rb \) consist \( B^{-2-}O^{-}\) network, built up from planar 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 properties changes upon network modification. The structural investigation of aluminum borate glasses have been studied by M.Kaur et al [8] and reported molar volume decreases with increase in density of glass. The structural investigation have been studied in \( Li_2O \cdot B_2O_3 \cdot Al_2O_3 \) 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 investigation of differential thermal analysis of lithium borate glasses with addition of Al2O3 as mixed former.

II. MATERIAL PREPARATION AND EXPERIMENTAL

The aluminum lithium borate glasses of composition 35Li2O : (65 – x)B2O3 : xAl2O3, \( (\text{Where} \ x = 0, 5, 10, 15, 20) \) 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\(^\circ\)C for two hours with heating rate 30\(^\circ\)C/min and molten material is quenched in aluminum mould at room temperature 27\(^\circ\)C. The samples were annealed at 200\(^\circ\)C for 2 Hrs in hot air oven. 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. FTIR of prepared samples were recorded by SHIMADZU FTIR spectrometer IR infinity1/8300 in the range 4000 - 400 \( \text{cm}^{-1}\) with resolution 4 \( \text{cm}^{-1}\).

III. RESULT AND DISCUSSION

A. Differential Thermal Analysis (TG-DTA)

The TG DTA curves of the sample is shown in Figure 1. 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 \( H_3B_3O_7 \) 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 $B_2O$. The final weight loss 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 $B_2O$. The 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 $B_2O$ and thereafter no appreciable weight loss 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 $B_2O$. The 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 transition temperature has been observed due to structural changes in the glasses.

The DTA curves of investigated samples (LB1A-LB5A) are shown in Figure 2. The values of glass transition temperature $T_g$, onset melting point temperature $T_o$ and offset melting point temperature $T_x$, obtained from graph are depicted in the Table 1. The effect of percentage of Al2O3 and former ratio on thermal transition data for these investigated sample is shown 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 Al2O3. The substitution of former Al2O3 in Li2O:B2O3 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 $\gamma$ 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 $T_x$ 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 $K_H$. It indicates lower devitrification tendency of this sample.
TABLE I
VALUES OBTAINED FROM TG DTA GRAPH OF LB1A-LB5A SAMPLES

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mole % Al₂O₃</th>
<th>Tₗ</th>
<th>Tₓ</th>
<th>Tₚ</th>
<th>Tᵣ</th>
<th>Tᵣg</th>
<th>∆Tₓ</th>
<th>γ</th>
<th>K – H</th>
</tr>
</thead>
<tbody>
<tr>
<td>LB1A</td>
<td>0</td>
<td>478</td>
<td>502</td>
<td>542</td>
<td>650</td>
<td>0.73</td>
<td>24</td>
<td>0.445</td>
<td>0.135</td>
</tr>
<tr>
<td>LB2A</td>
<td>5</td>
<td>522</td>
<td>555</td>
<td>625</td>
<td>760</td>
<td>0.68</td>
<td>33</td>
<td>0.432</td>
<td>0.138</td>
</tr>
<tr>
<td>LB3A</td>
<td>10</td>
<td>620</td>
<td>630</td>
<td>720</td>
<td>762</td>
<td>0.61</td>
<td>10</td>
<td>0.455</td>
<td>0.755</td>
</tr>
<tr>
<td>LB4A</td>
<td>15</td>
<td>720</td>
<td>755</td>
<td>770</td>
<td>767</td>
<td>0.71</td>
<td>35</td>
<td>0.499</td>
<td>0.744</td>
</tr>
<tr>
<td>LB5A</td>
<td>20</td>
<td>585</td>
<td>630</td>
<td>650</td>
<td>770</td>
<td>0.76</td>
<td>45</td>
<td>0.464</td>
<td>0.243</td>
</tr>
</tbody>
</table>

∆Tₓ. 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.

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 Al₂O₃. The GFA parameters ∆Tₓ 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.

REFERENCES