Effect of lithium fraction $f_{Li}$ on glass transition temperature $T_g$ and ionic conductivity $\sigma$ of lithium borosilicocititanate glasses

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Abstract. Three different lithium borosilicate glass systems with TiO$_2$ addition have been synthesized by melt quenching technique. The XRD was done for all glass samples to confirm their amorphous nature. Electrical conductivity ($\sigma$) of these glasses has been studied by dielectric impedance analyzer as a function of frequency at different temperatures in the range 480 to 650 K. Glass transition temperature $T_g$ for the glasses has been determined by using DTA. The density of all glass samples has been determined. It has been observed that the electrical conductivity increases with increasing content of TiO$_2$ which can be attributed to the modification of the structure by the addition of larger titanium ions. It is observed that higher lithium fraction $f_{Li}$ content glass series has highest conductivity. A good correlation is observed between the ionic conductivity, glass transition temperature and lithium fraction of the glasses. The analysis of IR spectra reveals the presence of Ti ions in tetrahedral TiO$_4$ units as well as creation of NBOs, which supports the conductivity results.

1. Introduction

Solid state lithium batteries have been given attention for their development because of their various application in the new generation of energy sources in microelectronic and information industry [1-3]. Lithium-ion batteries are giving choice to opt for high energy density, flexible, at the same time design with lightweight and longer lifespan than comparable battery technologies [4,5].

Lithium borosilicate glass systems are interesting to study as lithium concentration can be added to it upto large concentration and will produce stable glasses [6]. Generally high conductivity is observed in glasses with low melting point [7]. Eutectic composition are having lowest melting point which is useful to achieve high ionic conductivity. There are three different eutectic compositions in lithium borosilicate system [8]. Enhancement in conductivity in lithium borosilicate glasses with addition of TiO$_2$ has been attributed to the larger size of titanium ions which in turn reduces the rigidity of the network and expands the lattice [9]. The presence of small quantity of TiO$_2$ in the glass matrices is observed to enhance the glass forming ability and chemical durability of the glasses [10].

In the present work, three different series of lithium borosilicate glasses with addition of TiO$_2$ has been prepared. Among the three series, two are well known eutectic compositions in lithium
borosilicate glasses [8]. Thus, present work is aimed to study the effect of lithium fraction \( f_{Li} \) on glass transition temperature \( T_g \) and ionic conductivity \( \sigma \) of lithium borosilicotitanate glasses.

2. Experimental procedure

2.1. Glass preparation

The glass samples were prepared in three different series, which are represented as

Series-I: \( 30\text{Li}_2\text{O}:(70-x)/6/7\text{B}_2\text{O}_3:1/7\text{SiO}_2\):x\text{TiO}_2 \) with \( x = 0, 2.5, 5, 7.5 \) and 10 mol%

Series-II: \( 33.33\text{Li}_2\text{O}(66.67-x)/1.083/2.083\text{B}_2\text{O}_3:1/2.083\text{SiO}_2\): x\text{TiO}_2 \) with \( x = 0, 2.5, 5, 7.5, 10 \) and 12.5 mol%

Series-III: \( 40\text{Li}_2\text{O} (60-x)/2/3\text{B}_2\text{O}_3 :1/3\text{SiO}_2 \): x\text{TiO}_2 \) with \( x = 0, 2.5, 5, 7.5 \) mol%

(Series I and III are Eutectic composition)

For the glass preparation, an appropriate amount of AR grade \( \text{Li}_2\text{CO}_3 \) (E Merk), \( \text{B}_2\text{O}_3 \) (E Merk), \( \text{SiO}_2 \) (Fluka), and \( \text{TiO}_2 \) (Baker) were taken and mixed thoroughly. The conventional melt quenching technique (using platinum crucible) is used for glass synthesis. Annealing is done for all the quenched samples for 1hr at 537K.

2.2. Glass characterization

For all these samples, the glass transition temperature \( T_g \) was determined from the Differential Thermal Analysis (DTA) and the X-ray diffraction (XRD) patterns were recorded to confirm their amorphous nature. XRD analysis was performed using a PANalytical X'Pert PRO diffractometer (Cu-\( \alpha \) radiation \( \lambda =1.5405 \) Å). Diffraction patterns were acquired on finely ground samples for 20 values ranging from 5 to 80 degrees. The conductivity measurements were carried out using a Novocontrol Impedance Analyzer in the frequency range 10Hz – 10MHz and for the temperature ranging from 460K to 650K. The density of these glasses was measured using Archimedes principle with toluene as an immersion liquid. The molar volume \( (V_m) \) of each glass was evaluated from the density \( (\rho) \) and the molecular weight \( (M) \) according to \( V_m=M/\rho \). FTIR spectra were recorded on a MAGNA 550 spectrometer (Nicolet Instruments Corporation, USA) in the range 400-2000 cm\(^{-1}\).

3. Result and discussion

3.1. XRD

Figure 1 shows the XRD pattern for sample from Series-I containing 10 mol\% TiO\(_2\), which confirms the amorphous nature of glass. Similarly, the amorphous nature of other glass samples was confirmed. However, in order to avoid repetition XRD patterns are not included here.

![Figure 1: XRD pattern for the sample from Series-I containing 10 mol% TiO\(_2\)](image)

3.2. Transport number measurement

The contribution of ionic conductivity to the total conductivity can be determined by transport number measurements. The transport number calculated for glasses was found to be 0.999. The values of ionic transport number \( t_i \) were found to be greater than 0.99. This indicates that the glass samples in the present investigation are predominantly ionic conductors with negligible electronic conductivity.
3.3. Electrical conductivity

The bulk conductivity for all the samples was calculated from the complex impedance plots. It has been observed that the conductivity increases with temperature for all the samples. The activation energy $E_a$ was calculated from the Arrhenius plot. Figure 2 shows the variation of conductivity at 500K and activation energy with mol% TiO$_2$, for all series. In Series-I, II and III, Li$_2$O content is different and the addition of TiO$_2$ is done at the cost of formers. It is worthwhile to compare the conductivities of these series. It clearly shows that with addition of TiO$_2$, there is an enhancement in the conductivity of half an order of magnitude. The activation energy decreases with addition of TiO$_2$.

The base system contains BO$_4$ and SiO$_4$ tetrahedra to which non-bridging oxygens (NBOs) are attached. The oxidation state of Ti ions in SiO$_2$ has been reported [11] to be Ti$^{4+}$. In oxide glasses, Ti$^{4+}$ ions have been reported to take various coordinate structures as TiO$_4$, TiO$_5$ and TiO$_6$, resulting in the specific characteristics [12]. It has also been reported that below 9 wt% TiO$_2$, all of the Ti is fourfold coordinated and at higher concentrations (> 9 wt% TiO$_2$), some six fold coordinated Ti occur. Ti ions in tetrahedral TiO$_4$ units are regarded as network former (NWF) and those in octahedral TiO$_6$ units are considered as network modifier (NWM). It has been reported in case of TiO$_2$-SiO$_2$ glasses that some of the TiO$_4$ tetrahedra can replace SiO$_4$ tetrahedra [13].

In the present study, most of the glass samples have maximum concentration of TiO$_2$ is up to 10 wt%. When TiO$_2$ is added, initially Ti ions are presumed to be in tetrahedral units. Therefore, they may be going into the glass as network former and replacing some of the BO$_4$ and SiO$_4$ tetrahedra. With further addition of TiO$_2$, remaining Ti$^{4+}$ ions may sit in the voids thereby modifying the network. Thus, the system contains BO$_4$, SiO$_4$ and TiO$_4$ tetrahedra to which non-bridging oxygens (NBOs) are attached. The conduction in these glasses is due to successive jumping of Li$^+$ ions from one NBO to another. The conductivity is governed by the number of NBOs as well as the concentration of mobile Li$^+$ ions. It has been reported that when Ti$^{4+}$ ions are formed, the polarizability of oxygen atoms increases [14]. It is well known that higher the polarizability of anion, higher will be the mobility of mobile lithium ion attached to it. This explains the increase in conductivity with addition of TiO$_2$ as shown in figure 1. The variation of activation energy is opposite to that of conductivity. For few glass samples with higher concentrations of TiO$_2$ (> 9 wt %), some of the Ti$^{4+}$ ions may sit in the voids thereby modifying the network.

Figure 2: Comparison of variation of conductivity at 500K and activation energy with mol% TiO$_2$ in Series-I, II and III.
Table 1: Li$_2$O content and Lithium fraction $f_{Li}$ for Series-I, II and III.

| Series No. | Li$_2$O mol% | Lithium fraction $f_{Li}$ |
|------------|--------------|---------------------------|
| I          | 30           | 0.60                      |
| II         | 33.33        | 0.67                      |
| III        | 40           | 0.80                      |

Also, it can be seen from this figure that Series-III has highest conductivity among the three series. To understand these results the values of lithium fraction $f_{Li}$ [15] are given in the Table 1.

It should be noted here that for all the series TiO$_2$ is added at the cost of glass formers keeping Li$_2$O content constant. Conductivity increases in each series with addition of TiO$_2$ in spite of constant $f_{Li}$. As Li$_2$O content increases from Series-I to III, conductivity is found to be increasing which is attributed to increase in $f_{Li}$.

In series II, TiO$_2$ initially goes as a network former up to around 7.5 mol%, which results in an open structure, reducing the $T_g$. Beyond 7.5 mol% TiO$_2$, Ti ions may be in octahedral units and they may be entering the network as modifier. This could make the structure slightly rigid thereby increasing the $T_g$.

Figure 3 depicts the variation of glass transition temperature $T_g$ as a function of mol% TiO$_2$ for Series-I, II and III. It is observed that the $T_g$ is decreasing with TiO$_2$ addition in each series. Decrease in $T_g$ is more in case of Series-I which may be due to lower Li$_2$O content. Titanium being bigger in size causes the network expansion and reduces the rigidity of the glass. This in turn is responsible for weakening of the glass structure. In series II, TiO$_2$ initially goes as a network former up to around 7.5 mol%, which results in an open structure, reducing the $T_g$. Beyond 7.5 mol% TiO$_2$, Ti ions may be in octahedral units and they may be entering the network as modifier. This could make the structure slightly rigid thereby increasing the $T_g$.

Decrease in $T_g$ with addition of TiO$_2$ supports the conductivity results as discussed in above section. As one moves from Series-I to III, the lithium fraction is gradually increasing, the $T_g$ values are decreasing and ionic conductivity increasing. The glass samples of Series-III having relatively higher lithium fraction exhibit lower values of $T_g$ (indication of weakened glass structure) and higher ionic conductivity. Thus, there is a very good correlation of lithium fraction, glass transition temperature and ionic conductivity observed in these glasses.

Table 2 shows the density $\rho$ (g/cc) and molar volume $V_m$ (cm$^3$.mol$^{-1}$) for glass samples of Series III, as a function of mol% TiO$_2$. To get more insight into the glass network, the average boron-boron separation $d_{\text{B-B}}$ has also been calculated [16] which is shown in Table 2.
Table 2: Variation of density $\rho$, molar volume $V_m$ and Boron-Boron distance $d_{<B-B>}$ with mol\% TiO$_2$ for the glasses of Series-III.

| mol \% TiO$_2$ | Density $\rho$ (g/cc) | Molar volume $V_m$ (cm$^3$.mol$^{-1}$) | Boron-Boron distance $d_{<B-B>}$ (nm) |
|----------------|-----------------------|----------------------------------------|---------------------------------------|
| 0              | 2.4990                | 20.74                                  | 31.14                                 |
| 2.5            | 2.4399                | 21.38                                  | 31.18                                 |
| 5              | 2.3859                | 22.00                                  | 31.20                                 |
| 7.5            | 2.1996                | 24.02                                  | 31.85                                 |

Decrease in density and increase in molar volume with addition of TiO$_2$, indicates reduction in rigidity of the glass structure which is supported by decrease in $T_g$. It has been reported earlier that, enhancement in conductivity is due to increase in molar volume of the glass [17]. The increase in molar volume is associated with an increase in the number of interstices around the mobile ion, which causes increase in the jump probability of the mobile ion giving rise to an enhancement in conductivity. This result is further supported by Boron-Boron distance $d_{<B-B>}$, which increases slightly, as shown in the Table 2. Thus, there is a good correlation of the glass transition temperature, molar volume and density results with electrical conductivity.

Figure 4: FTIR Spectra for the glasses of Series-III.

Figure 4 shows the FTIR spectra for the glasses of Series-III. Three major groups of bands (i) 1200-1500 cm$^{-1}$ (due to the stretching relaxation of the B-O bond of the trigonal BO$_3$ units) (ii) 800 - 1200 cm$^{-1}$ (due to the B-O stretching of tetrahedral BO$_4$ units) (iii) 600 – 800 cm$^{-1}$ bending vibrations of various borate segments are observed[18].

With the addition of TiO$_2$, the band at 910 cm$^{-1}$ (B-O bond vibration in BO$_4$ units) splits into two bands, one band is obtained at 870 cm$^{-1}$ (stretching vibrations of tetrahedral BO$_4$ units [18- 20]) and
another at 950 cm\(^{-1}\) (stretching vibrations of TiO\(_4\) units [21,22]). It is also observed that the intensity of IR spectra in the region between 800-1100 cm\(^{-1}\) (BO\(_4\) groups [18- 20]) decreases. This shows that there is formation of TiO\(_4\) tetrahedra at the expense of BO\(_4\) tetrahedra. Similar results have been observed in Li\(_2\)O-B\(_2\)O\(_3\)-LiCl-Al\(_2\)O\(_3\) glasses [23]. The band obtained around 700 cm\(^{-1}\) is attributed to bending of B-O-B linkage in the borate network. Earlier studies on TiO\(_2\) containing glasses reveal that, bands between the region 700 and 800 cm\(^{-1}\) are attributed to Ti-O stretching in tetrahedral TiO\(_4\) positions [24, 25]. It is observed that with increasing TiO\(_2\) concentration, the band at 700 cm\(^{-1}\) shift to higher wave number side and increases in intensity. This result indicates that there is possibility of the formation of single B-O-Ti framework in the glass.

The band located between 1246-1207 cm\(^{-1}\) is assigned to the stretching vibrations of the B-O bonds of BO\(_4\) units involving mainly the linkage oxygen connecting different groups. The band between 1479-1429 cm\(^{-1}\) is assigned to antisymmetrical stretching vibrations with three NBOs of the B-O-B groups. The band at 1375 cm\(^{-1}\) (B-O asymmetric stretching vibrations in BO\(_4\) units) shift to the higher wave number side and merges into the band located at 1429 cm\(^{-1}\) thereby increasing its intensity. This suggests that there is increase in number of NBOs [18] due to the modification of borate network. These results are found to be supporting the conductivity results.

4. Conclusion

Ionic conductivity of lithium borosilicate glasses increases with addition of TiO\(_2\) has been studied in three different series. Addition of TiO\(_2\) in lithium borosilicate network causes enhancement in conductivity. The enhancement in conductivity is attributed to the weakening of the structure which increases the mobility of Li\(^+\) ions due to addition of TiO\(_2\) as well as increase in the Li fraction causes highest conductivity in series III. A good correlation is observed between the ionic conductivity, glass transition temperature and lithium fraction of the glasses. The analysis of IR spectra reveals the presence of Ti ions in tetrahedral TiO\(_4\) units as well as creation of NBOs, which supports the conductivity results.

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