# Enhancement in electrical conductivity of $Li_2O : B_2O_3 : V_2O_5$ glasses

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**Abstract.** The study of electrical conductivity of $30Li_2O : (70 - x) B_2O_3 : xV_2O_5$ glass samples has been carried out. The results have been explained by dividing the temperature range into two regions. In region I, conductivity shows Arrhenius behaviour for all the samples. The conductivity increases with addition of $V_2O_5$. The results have been explained in the light of Anderson and Stuart Model. In region II, an anomalous enhancement in the conductivity is observed for all the samples up to certain temperature beyond which the conductivity decreases. The enhancement in the conductivity in the annealed glass sample has been attributed to nanocrystallization.

**Keywords.** Lithium conducting glasses; electrical conductivity; nucleation and crystallization; glass transition temperature.

## 1. Introduction

Lithium ion conducting glasses and glass–ceramics have enormous potential for utilization in electrochemical devices (Ravaine 1980; Minami 1987; Linford 1988; Deshpande 1995; Angell 1998). The main hurdle in this area is the availability of solid electrolyte with high ionic conductivity. It has been observed that, the efforts to enhance ionic conductivity of lithium conducting glasses are always associated with their instability. The conversion of glass into glass–ceramic is likely to increase the stability (McMillan 1964; Kingery et al 1976).

Most of the studies of lithium conducting glasses carried out so far have been restricted to temperature range much below the glass transition temperature (Meikhail et al 1993; Kluvanek et al 2007). On the other hand, the electrical conductivity of glass–ceramics has been studied after conversion of glass into glass–ceramics (Johnson et al 1975; Jie Fu 2000). Nevertheless a few reports (Fang 1982; Shixun et al 1991; Sukeshini and Harihararn 1993) are available on the anomalous conductivity behaviour of the glassy systems above the glass transition temperature, $T_g$. The enhancement in the conductivity by two orders has been reported above glass transition temperature due to nucleation and decrease in the conductivity above crystallization temperature due to massive crystallization (Adams et al 1994; Gedam et al 2005). The enhancement in the electrical conductivity in lithium vanadate glasses by nanocrystallization has been reported earlier (Garbarczyk et al 2004). With a view to verify whether a similar enhancement in the conductivity behaviour is ob-

served for lithium borate glasses above the $T_g$, an attempt has been made to study the electrical conductivity of $Li_2O : B_2O_3 : V_2O_5$ glasses as a function of temperature, in the present work.

## 2. Experimental

The glass series with general formula, $30Li_2O : (70 - x) B_2O_3 : xV_2O_5$, with $x$ varying from 0–20 at an interval of 5 mol% was prepared by conventional quenching technique. Appropriate amounts of lithium carbonate of AG Fluka, $B_2O_3$ (E-Merck) and $V_2O_5$ (Fluka AG) were taken and mixed thoroughly. The mixture was then put in a platinum crucible and heated to melt in an electric furnace. The melting point of the glasses ranged from 1100–1150 K depending on the composition. The melt was then maintained at 40 K above the melting point for 2 h with frequent stirring to ensure homogeneity. The melt was then quenched in an aluminium mould at room temperature to get rectangular samples. The quenched samples were then annealed for 2 h at 525 K. The glass transition temperature ($T_g$) and crystallization temperature ($T_c$) were determined with the help of differential thermal analyser (Mettler Toledo). The impedance measurements were carried out as a function of temperature in the frequency range 100 Hz–20 MHz using High Resolution Dielectric Analyzer (Novocontrol make).

## 3. Results and discussion

Variation of conductivity as a function of $10^3/T$ for the glass samples of the series $30Li_2O : (70 - x)B_2O_3 : xV_2O_5$ is shown in figure 1. For all the samples, it is observed

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that the conductivity shows Arrhenius behaviour up to certain temperature beyond which there is an anomalous increase in conductivity and subsequent decrease in conductivity. For the sake of understanding the results, the conductivity behaviour is grouped into two regions of temperature. The region I (below $T_g$) in which conductivity shows Arrhenius behaviour and region II (above $T_g$), where an anomalous behaviour is seen.
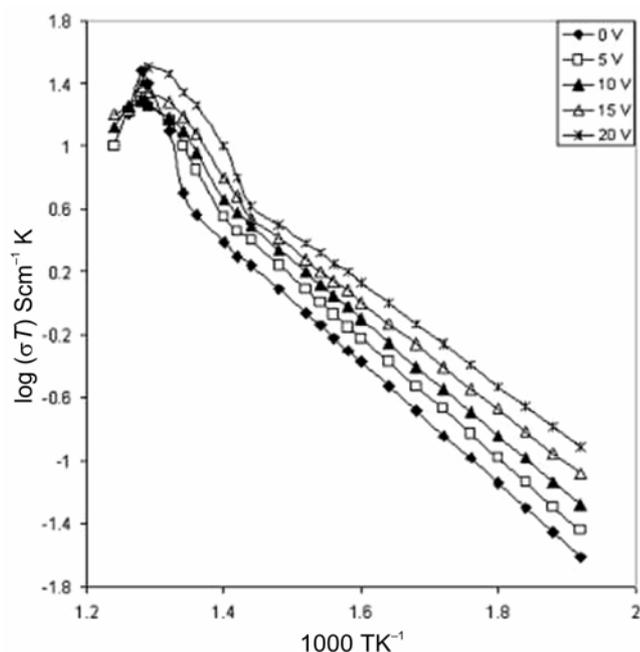


**Figure 1.** Variation of conductivity as a function of temperature.
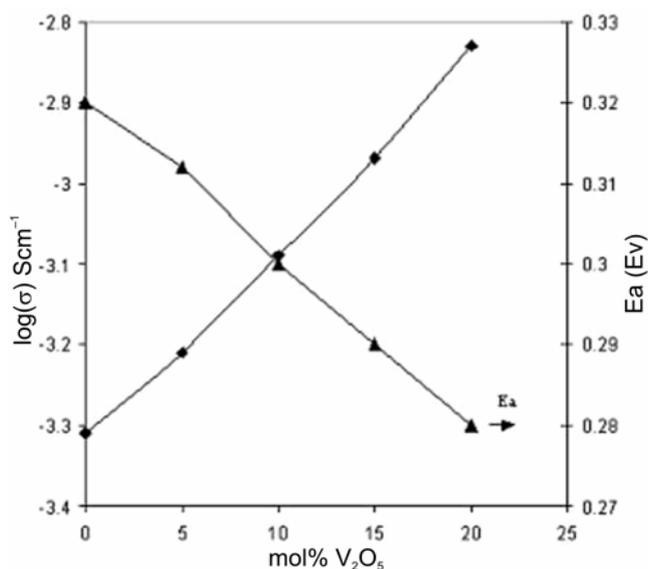


**Figure 2.** Variation of conductivity and activation energy vs mol% $V_2O_5$.

In region I, the variation of conductivity at 650 K and activation energy as a function of mol% $V_2O_5$ has been depicted in figure 2. From this figure it is evident that the conductivity of $Li_2O:B_2O_3$ system increases with the addition of $V_2O_5$. The activation energy shows opposite behaviour to that of conductivity. The variation in conductivity could be explained on the basis of the Anderson and Stuart model (Anderson and Stuart 1954). According to this model, as the glass former ion is substituted by another glass former ion, the average interionic bond distance becomes larger or smaller according to whether the substituting ion is larger or smaller. In the present case, the ionic radius of $V^{5+}$ is bigger than that of $B^{3+}$, therefore,
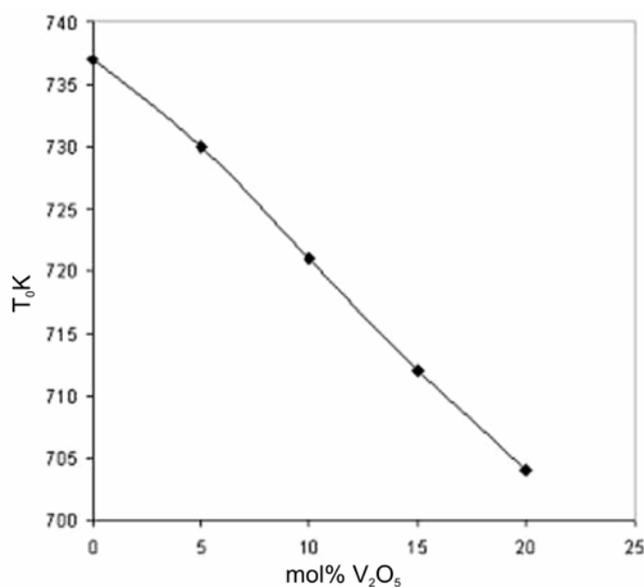


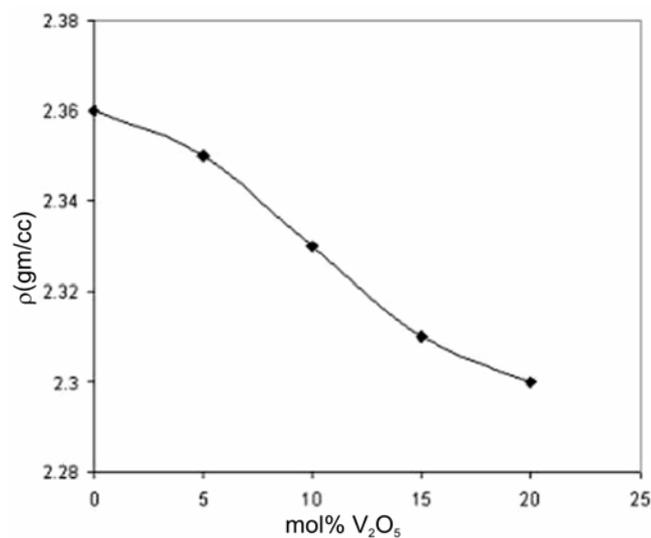**Figure 3.** Variation of $T_g$ vs mol% $V_2O_5$.



**Figure 4.** Variation of density vs mol% $V_2O_5$.

the addition of $V_2O_5$ expands the lattice structure and hence enhances the mobility of lithium ions. This is also supported by the decrease in glass transition temperature ($T_g$) and density ($\rho$) as displayed in figures 3 and 4. Similar variation in the conductivity and glass transition temperature has been reported earlier in lithium vanadium phosphate glasses (Garbarczyk *et al* 2002). An increase in conductivity with the addition of $V_2O_5$ is also associated with increase in the number of non-bridging oxygens. Similar results have been reported earlier (Mekki *et al* 2003) who have used X-ray photoelectron spectroscopy to determine the number of non-bridging oxygens. The increase of non-bridging oxygens would make the structure more loose. This further supports the results of $T_g$ and density of glasses as shown in figures 3 and 4 which helps to enhance the conductivity.

In region II (figure 1), it is observed that for all samples of the series, there is an anomalous enhancement in the conductivity above glass transition temperature, $T_g$. The conductivity becomes maximum at certain temperature known as peak temperature, $T_p$ and then decreases as the temperature is increased further. An anomalous increase in the conductivity above glass transition temperature has been reported (Adams *et al* 1994) in the silver conducting glasses. According to this report an anomalous increase in the conductivity is due to nucleation and subsequent decrease in the conductivity is due to crystallization of the glasses. Table 1 shows $T_g$ and $T_p$ for all the samples of the series. It can be seen from this table that the temperature, $T_p$, at which conductivity is maximum is different
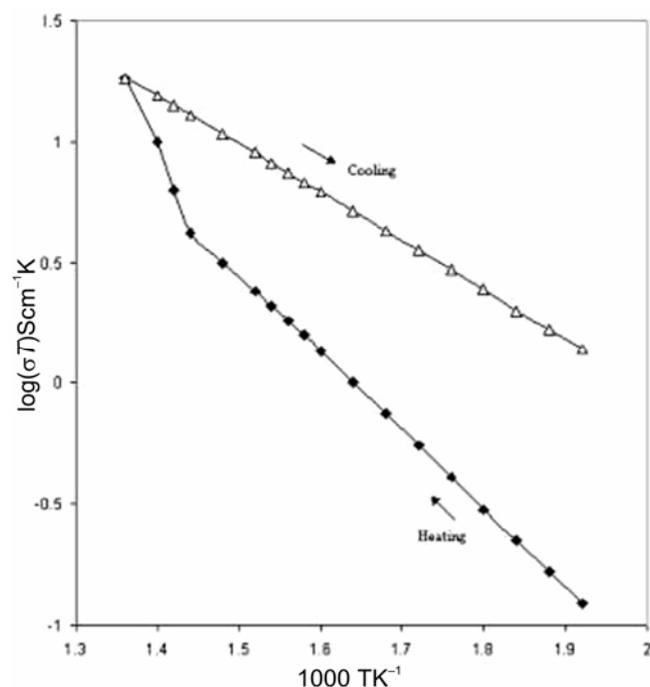
for different samples. Similar anomalous enhancement in the electrical conductivity of lithium borate glasses containing ZnO and $Al_2O_3$ has been observed recently (Gedam *et al* 2005; Gedam and Deshpande 2006). Thus it is certain that in the lithium borovanadate glasses when the temperature increases beyond $T_g$, an anomalous enhancement in the conductivity by more than one order of magnitude is observed due to nucleation.

It was thought interesting to see whether by subjecting the glass samples to a controlled heat treatment the crystallization can be controlled, which in turn, would give enhanced conductivity. Hence the conductivity of all the glass samples was measured during heating cycle at a controlled rate up to temperatures, 20 K below the peak temperature. The sample was annealed at this temperature for 3 h and then allowed to cool in a controlled manner and its conductivity was measured during cooling cycle.

Figure 5 shows the temperature dependence of conductivity for glass sample containing 10 mol% $V_2O_5$ during heating and cooling cycles. The conductivity shows Arrhenius behaviour below $T_g$ and it shows an enhancement in the conductivity above $T_g$ up to annealing temperature. On cooling, the temperature dependence of conductivity followed the Arrhenius plot but with lower activation energy than that during heating. The values of
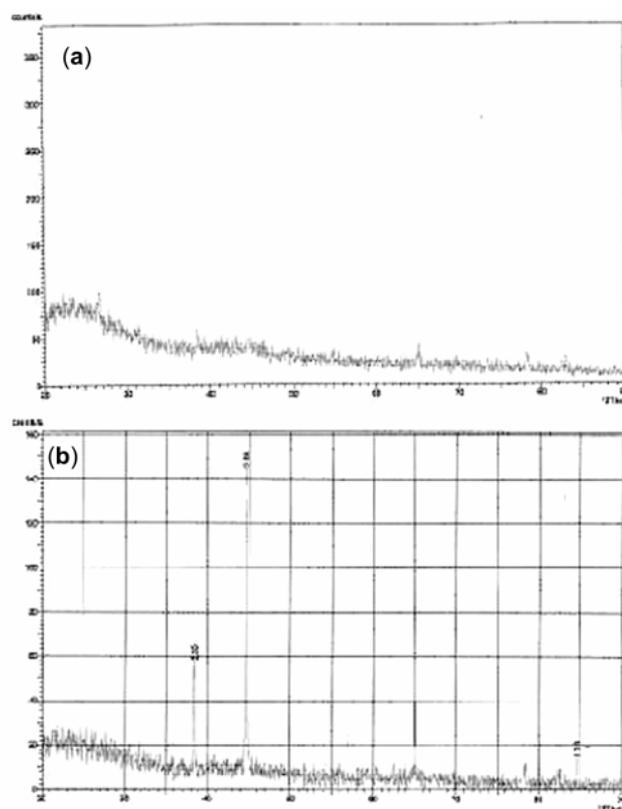


**Figure 5.** Variation of conductivity with temperature of annealed glass sample.



**Figure 6.** (a) XRD pattern of glass sample containing 10 mol% $V_2O_5$ and (b) XRD pattern of annealed glass sample containing 10 mol% $V_2O_5$.

conductivity during cooling cycle are higher than those observed during heating cycle by more than half an order of magnitude.

This enhancement in the conductivity observed during cooling cycle may be attributed to structural changes in annealed glass sample wherein, the possibility of nano-crystallization was expected. In order to confirm the nanocrystallization in the glass, the XRD of this sample was recorded before and after annealing and the results are shown in figures 6(a) and (b), respectively. Figure 6(a) does not show any peak in the XRD which confirms the
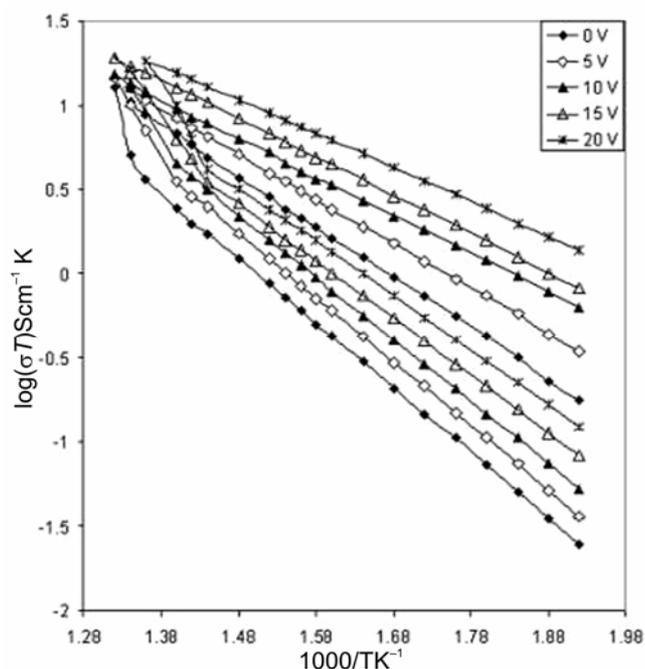


**Figure 7.** Variation of conductivity with temperature of annealed glass sample.

**Table 1.** $T_g$ and $T_p$ values of glass samples.

| Mol% $V_2O_5$ | $T_g$ (K) | $T_p$ (K) |
|---|---|---|
| 0 | 737 | 780 |
| 5 | 730 | 770 |
| 10 | 721 | 775 |
| 15 | 712 | 786 |
| 20 | 704 | 773 |

**Table 2.** Crystallite size in samples after annealing.

| Mol % $V_2O_5$ | $t$ (nm) |
|---|---|
| 0 | 45 |
| 5 | 46 |
| 10 | 35 |
| 15 | 33 |
| 20 | 34 |

glass formation. The XRD pattern of the glass sample depicted in figure 6(b) shows a number of peaks corresponding to crystalline phase. However, there is still a considerable amount of amorphous phase present. The average size of crystallites was estimated from the width of diffraction peak using the Scherrer formula

$$t = 0 \cdot 9 \lambda / B \cos \theta,$$

where $t$ is the size of crystallites, $\lambda$ the wavelength of X-rays, $B$ the full width of peak at half maximum intensity and $\theta$ the angle.

The average crystallite size was found to be 35 nm. Similar results were observed for all other samples during heating and cooling cycles which are displayed in figure 7. All the samples were annealed at temperature 20 K below $T_p$ and they were annealed at this temperature for 3 h. The values of average crystallite size ($t$) in the annealed glass samples determined from XRD pattern are given in table 2.

It is evident from this table that for all the samples after annealing at temperature above $T_g$ but 20 K below $T_p$, there occurs nanocrystallization which is responsible for the enhancement in the conductivity. Similar increase of electrical conductivity due to nanocrystallization has been observed recently (Garbarczyk *et al* 2004) in $Li_2O$ : $V_2O_5$ : $P_2O_5$ glass system. According to them since the average size of these crystallites is small, the interface between crystalline and amorphous phases is very extensively ramified and it strongly influences overall electrical properties of the nanomaterial.

## 4. Conclusions

From the present investigation it can be concluded that, in region I (below $T_g$) the electrical conductivity in $Li_2O$ : $B_2O_3$ : $V_2O_5$ glass system increases with the addition of $V_2O_5$ and this can be understood on the basis of Anderson and Stuart model. The lowering of glass transition temperature and density of the glass samples with increase of $V_2O_5$ content has been attributed to the increased number of non-bridging oxygens which weakens the glass structure. In region II, an enhancement in the conductivity in the annealed glass sample is observed due to nanocrystallization.

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