Transport properties of ferroelectric (lead titanate) doped zinc-borate glasses

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Ferroelectric doped zinc-borate glasses of the composition (1-x) \([40 \text{ZnO} - 60 \text{B}_2\text{O}_3]\) + x \(\text{PbTiO}_3\), with 
\(x = 0.0, 0.05, 0.1, 0.15, 0.2\) were prepared. Physical properties such as density \((d)\), molar volume \((V)\), hopping distance \((R)\), number of zinc ions per cc \((N)\), and polaron radius \((r_p)\) were reported. DC-conductivity was measured between 443 K to 573 K. From this, two graphs \((a) - \log \sigma\) versus \(1/T\) and \((b) - \log \mu\) versus \(1/T\) were plotted. Activation energy \(W\) was determined from the plots. Effect of ferroelectric doping on the hopping conduction was studied. Polaron bandwidth \((J)\) was found to satisfy the inequality for all samples thus suggesting adiabatic hopping conduction mainly governed by the activation energy.

Study of transport properties of glasses gives an insight of the glass structure. Further they are important from their industrial application point of view. Transport properties provide information about the type of hopping conduction. The dc-conductivity occurs by the hopping of small polarons between the occupied to unoccupied valence states and the activation is temperature dependent. In semiconducting glasses two types of hopping conduction are observed namely (i) adiabatic and (ii) nonadiabatic. Adiabatic conduction is mainly governed by the activation energy.

Sayer and Mansingh\(^1\) studied conductivity and other parameters of many oxide glasses. Dhote et al.\(^2\) observed adiabatic conduction in zinc-bismuth glasses. Temperature dependent activation was found responsible for conduction in bismuth - borate glasses.\(^3\) The electrical conduction of the glass composition 40 ZnO - 60 B\(_2\)O\(_3\) has been studied\(^4\). The results of their studies of rare earth ions doped lithium fluoroborate glasses have been found to yield valuable information.\(^5,6\) Lead titanate, a ferroelectric in nature is added as a dopant to 40 ZnO - 60 B\(_2\)O\(_3\) glass and the effect of dopant on physical properties and hopping mechanism is studied.

Theory

The dc electrical conductivity of semiconducting oxide glasses for the hopping of polarons in a non-adiabatic approximation is given\(^7\) by

\[
\sigma = \frac{N e^2 v c (1-c)}{kT} \exp(-2\alpha R) \exp(-W/kT) \quad \text{... (1)}
\]

where \(N\) is number of zinc ions per unit volume, \(\alpha\) is electron wave function decay constant, \(R\) is hopping distance, \(c\) is fraction of sites occupied by polarons., \(W\) is activation energy, \(v\) is phonon frequency and \(k\) is Boltzmann’s constant.

Polaron hopping energy \(W_H\) is given by

\[
W_H = W_{p}/2
= e^2/4\varepsilon_p (1/r_p^2 - 1/R) \quad \text{... (2)}
\]

\(1/\varepsilon_p = 1/\varepsilon_m\), here \(\varepsilon_m\) at a frequency of 100 kHz is used for calculation.

The polaron radius \(r_p\) is given by

\[
r_p = 1/2 (\pi / 6)^{1/3}.R \quad \text{... (3)}
\]

And \(R\) is hopping distance given by

\[
R = (M/N_0 \text{dexp}) \quad \text{... (4)}
\]

where \(M\) is molecular weight, \(N_0\) is Avagadro’s number and \(\text{dexp}\) is density of glass.

For knowing the nature of hopping conduction (adiabatic or non-adiabatic), the condition is that the polaron band width should satisfy the inequality

\[
J > (2kTW_H/\pi)^{1/4}(h\nu/\pi)^{1/2} \quad \text{for adiabatic hopping} \quad \text{... (5)}
\]

and \(J < J^*\) for non-adiabatic hopping

\[
J^* = (2kTW_H/\pi)^{1/4}(h\nu/\pi)^{1/2} \quad \text{... (6)}
\]

Similarly for confirmation of adiabatic conduction a graph is plotted between \((- \log \sigma)\) and activation energy \(W\) at constant temperature \(T\) for all samples.\(^1,8\) The graph is a linear one and the slope of which, is
1/kT, using value of Boltzmann's constant, value of T can be determined. Another method suggested by Emin and Holstein for confirmation of adiabatic conduction is applied. Emin and Holstein derived an expression for the mobility in the case of adiabatic conduction as

$$\mu = \frac{\sigma}{N_e} = \frac{4}{3} (e W e R/kT)^2 \exp \left[\frac{(W_H - J)}{kT}\right]$$

where \(\mu\) is mobility. The plot of \((-\log \mu)\) versus \(1/T\) gives the value of activation energy \((W = W_H - J)\).

**Experimental Procedure**

Glasses under consideration were prepared by mixing appropriate amount of AR grade ZnO, H₃BO₃ and PbTiO₃ (prepared in the laboratory). A homogeneous mixture was prepared by repeated grinding. It was fired in a fire clay crucible at 1223 K for two hours in a muffle furnace. The glasses were formed by quenching the melt on a steel plate held at room temperature. The samples were then annealed at 473 K for an hour. The amorphous nature of glasses was confirmed by XRD study. Samples were in the form of pellets. They were polished by emery paper (No. 100) and a quick drying silver paint was applied on either faces to act as electrodes. Then the samples were baked at 423 K for half an hour in order to remove mechanical stresses due to polishing and to stabilize the contacts. The samples were named as A, B, C, D and E for \(x = 0, 0.05, 0.1, 0.15\) and 0.2 respectively. Density of the samples was measured by Archimedes principle. Benzene was used as buoyant liquid.

The resistance of the samples was measured by commonly used voltage drop method. The samples were placed in a suitable holder and then in a furnace. The measurements were carried out in temperature range 443 - 573K.

DC conductivity was determined from resistance, thickness and area of silver electrode of sample. A graph was plotted between \((-\log \sigma)\) versus \(1/T\) for all the samples (Fig. 1). While another graph is plotted between de-conductivity and molar percentage of PbTiO₃ at constant temperature (Fig. 2) from which effect of dopant on conductivity is clearly observed.

### Table 1 — Physical parameters of \((40\text{ZnO}-60\text{B}_2\text{O}_3 \pm (1-x)\text{PbTiO}_3\)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>(x)</th>
<th>(d) g cm⁻³</th>
<th>(V) cm³ mol⁻¹</th>
<th>(R) Å</th>
<th>(N) (\times 10^{22}) cm⁻³</th>
<th>(R_p) Å</th>
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<tr>
<td>1</td>
<td>0</td>
<td>3.4209</td>
<td>21.7199</td>
<td>3.3051</td>
<td>2.77</td>
<td>1.3316</td>
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<td>2</td>
<td>0.05</td>
<td>3.4808</td>
<td>21.3634</td>
<td>3.2867</td>
<td>2.8184</td>
<td>1.3242</td>
</tr>
<tr>
<td>3</td>
<td>0.10</td>
<td>3.5022</td>
<td>21.244</td>
<td>3.2808</td>
<td>2.8338</td>
<td>1.3218</td>
</tr>
<tr>
<td>4</td>
<td>0.15</td>
<td>3.4829</td>
<td>21.7362</td>
<td>3.2876</td>
<td>2.816</td>
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<tr>
<td>5</td>
<td>0.20</td>
<td>3.4745</td>
<td>21.4423</td>
<td>3.2909</td>
<td>2.8076</td>
<td>1.3259</td>
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</table>

### Table 2 — Transport properties of \((40\text{ZnO}-60\text{B}_2\text{O}_3 \pm (1-x)\text{PbTiO}_3\)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>(x)</th>
<th>(W) (eV) (from Fig. 1)</th>
<th>(W_p) (eV)</th>
<th>(W_H) (eV)</th>
<th>(W) (eV) (from Fig. 3)</th>
<th>(J) (eV)</th>
<th>(J^*) (eV)</th>
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<tr>
<td>1</td>
<td>0</td>
<td>0.0639</td>
<td>0.8856</td>
<td>0.4428</td>
<td>0.008442</td>
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<tr>
<td>2</td>
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<td>0.009164</td>
<td>0.3611</td>
<td>0.1806</td>
<td>0.005257</td>
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<tr>
<td>3</td>
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</tr>
<tr>
<td>4</td>
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<tr>
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<td>0.1421</td>
<td>0.01055</td>
<td>0.1334</td>
<td>0.00908</td>
</tr>
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</table>
Density, molar volume, hopping distance, number of zinc ions per cc.s and polaron radius are calculated and are presented in Table 1. The density is found to increase with the doping percentage but the change is not linear. The molar volume is also decreasing with doping from sample A to E. It is a small polaron model since the value of $r_p$ is around 1.3 Å. Similar trend was observed in lithium fluoroborate glasses for varying percentage of lead oxide dopant.\(^\text{13}\)

From Table 2, it is observed that the values of $J$ are greater than the values of $J^*$ for all samples. Which suggests that the hopping is adiabatic in nature.

From the plot of (-log $\sigma$) and $W$ (Fig. 3), the value of $T$ is calculated as 559 K while the actual value is 533 K which is in close agreement thus confirming the adiabatic hopping conduction. Further it is mainly controlled by the activation energy only.\(^\text{14}\)

Fig. 4 shows graph of (-log $\mu$) versus $1/T$. From Table 2, it appears that the values of activation energy calculated from the slopes of the plots of Fig. 1 and Fig. 4 are equal but they differ with polaron hopping energy ($W_H$) which confirms the adiabatic hopping conduction.

**Conclusion**

The adiabatic hopping conduction is observed here in lead titanate doped zinc borate glass. The small
polaron model is applicable. The conductivity changes with ferroelectric oxide doping. Lead titanate acts as a glass modifier because of which the conductivity increased at higher temperatures. However, the rise in conductivity so also the mobility was not uniform at lower temperature for B and C. The possible reason may be that the modifier gets bounded in the glass structure and becomes less mobile than the glass former. And on getting sufficient thermal activation the conductivity and mobility increased at higher temperature.

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References