Electrical characterization of Pr$^{3+}$ containing lithium borate glasses by impedance spectroscopy

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ABSTRACT

The role Pr$^{3+}$ ions in the lithium borate glasses have been investigated by electrochemical impedance spectroscopy technique. The glasses were prepared by conventional melt quench technique with formula 27.5 Li$_2$O-(72.5-X) B$_2$O$_3$-X Pr$_2$O$_3$ (where, X= 0.5, 1, 1.5 and 2). It is observed that the conductivity of the glasses decreases with the addition of Pr$^{3+}$ ions which was correlated with increase in the activation energy of the glasses. The observed conductivity behavior in the present study is mostly governed by the Pr$^{3+}$ as it has higher molecular weight as compared to other component in the glass system. Insight of conduction mechanism was revealed by the scaling of modulus and conductivity data of the prepared samples. Scaling confirms that the conduction mechanism is compositional dependent. Based on the present study it is possible to use and modified these glasses as an insulating and dielectric material. Copyright © 2016 VBRI Press.

Keywords: Li$^+$ conduction; glasses; impedance spectroscopy; rare earths.

Introduction

There is a phenomenological interaction between good solid electrolytes and characterization technique for these electrolytes. The impedance spectroscopy is one of the best known tools to study and characterize the electronic properties of the materials (e.g. amorphous, crystalline and liquid) [1]. This technique based on the frequency response of the material to a change in impedance. This technique widely used to explore conductivity, relaxation processes and dielectric response of the materials [1-6].

The lithium based glasses are the best known ion conducting material and have a potential application as solid state batteries [7-20]. Although these glasses offer less ionic conductivity as compared to Ag$^+$ ion based glasses but high electropositive nature of Li$^+$ ions have advantageous for solid state batteries [7]. Glass former e.g. SiO$_2$, P$_2$O$_5$, V$_2$O$_5$, B$_2$O$_3$, SeO$_2$ and TeO$_2$ with lithium as modifier shows the ionic conductivity [9]. Among these glass systems, lithium borate glasses are widely studied by the researcher as it offers wide composition range, easy formability and good rare earth solubility [10-11]. The complexity and functionality of these glasses mostly govern by the Li$^+$ content and the boron anomaly [10-20]. The conductivity of these glasses increases with the increase in Li$^+$ content. Addition of another glass former in lithium borate glasses also increases the conductivity which term as mixed former effect. There are various reports available on the electrical properties of lithium borate glasses [11-20]. Thakur et al. [21] recently reported the effect of BaTiO$_3$ on Dy$_2$O$_3$ containing glasses on the electrical properties of Lithium borate glasses. These glasses follow the correlated barrier hopping model (CBH). Scaling shows perfect overall data on single master curve indicates relaxation dynamics in these glasses. Yusub et al. [22] investigated the effect of MnO on the Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$ glasses where semiconducting nature of the glasses increases with the addition of MnO.

Rare earth oxides are the technically important class in the periodic table as they offer the ample range of functional materials like high-temperature superconductors, ferroelectric and optical materials [23]. Rare earth oxides are chemically active and thermally stable. Their chemical activity is interesting to study because of partially filled 4f electron shells [24]. Despite of their unique chemical behavior, the effect of rare earth addition on electrical properties of glasses is not well studied by the researcher. There are some reports available on electrical properties of rare earth oxide containing glasses [25-27].

Earlier we report spectroscopic properties of Pr$^{3+}$ ions containing lithium borate glasses that show their usefulness in solid state light application [28] and this manuscript is a continuation of previous work. There are no reports available on the electrical properties of Pr$^{3+}$ ions containing lithium borate glasses. The purpose of this paper to understand the conduction phenomenon and effect of Pr$^{3+}$ ions the lithium borate glasses as it is necessary to understand the fundamentals before any practical applications. We reported the data about conductivity, relaxation properties and scaling behavior of Pr$^{3+}$ ions containing lithium borate glasses.
Experimental

Materials

The glasses were prepared by convention glass quenching technique with general formula 27.5 Li₂O-(72.5-X) B₂O₃-X Pr₆O₁₁. High purity chemicals lithium carbonate (Li₂CO₃), boron trioxide (B₂O₃) and dysprosium oxide (Pr₆O₁₁) Merck Germany make of purity 99.99% were used as starting materials in the present study.

Method

Appropriate quantity of these chemicals weighs and mixed in acetone to ensure homogeneity. Mixture was then transferred to programmable furnace for melting. The mixture was melted at 1253 K and then quench quickly in metallic mold. The bulk sample further transferred to annealing furnace to remove the thermal stresses. Bulk glass samples were cut and polished for Impedance study.

Characterizations

Electrode contact were made by applying silver paint on the parallel faces of the glasses and then placed in between two silver electrodes after checking contact and continuity. Impedance measurements were performing on the using high resolution dielectric analyzer (Novocontrol Make) in the frequency range 2 mHz to 20 MHz. All the measurements were done by computer controlled WinDETA software. To determine the conductivity physical dimension of the sample and bulk resistance from impedance plot was taken in to account. DTA for all glass samples were recorded using Perkin-Elmer Diamond Thermal Analyzer with heating rate of 10 °C/min for determining glass transition temperature (Tg).

Results and discussion

The impedance spectra were measured over the temperature range of 673 K to 423 K. DC resistances was determined from the impedance plot and by using the physical dimension of the samples conductivities were determined [10]. The bulk ionic conductivities from measured impedance follow the Arrhenius equation as expected (Fig. 1).

![Fig. 1. Variation of conductivity with temperature for glasses.](image)

![Fig. 2. Variation of conductivity and activation energy with Pr₆O₁₁.](image)

<table>
<thead>
<tr>
<th>mol % Pr₁₁O₆</th>
<th>Glass transition temperature (Tg)</th>
<th>E_{dc} (eV)</th>
<th>E_{DC} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (PR0)</td>
<td>755 K</td>
<td>0.3791</td>
<td>0.3899</td>
</tr>
<tr>
<td>0.5 (PR1)</td>
<td>759 K</td>
<td>0.3828</td>
<td>0.4075</td>
</tr>
<tr>
<td>1 (PR2)</td>
<td>763 K</td>
<td>0.3896</td>
<td>0.4153</td>
</tr>
<tr>
<td>1.5 (PR3)</td>
<td>767 K</td>
<td>0.4221</td>
<td>0.4385</td>
</tr>
<tr>
<td>2 (PR4)</td>
<td>770 K</td>
<td>0.4442</td>
<td>0.4464</td>
</tr>
</tbody>
</table>

To study the relaxation behavior, electric modulus formalism was introduced and discussed [29, 30]. Electric modulus is defined as [31-32]:

\[ M^*(\omega) = \frac{1}{\varepsilon^*} \]

\[ M^*(\omega) = \frac{\varepsilon'(\omega)}{[\varepsilon^*(\omega)]} - i \frac{\varepsilon''(\omega)}{[\varepsilon^*(\omega)]} \]

\[ M^*(\omega) = M'(\omega) + iM''(\omega) \]
where, $M'$ and $M''$ are real and imaginary part of modulus.

**Fig. 3** shows the variation of real part of an electric modulus ($M'$) with frequency for PR 3 glass sample as a representative. From the figure, it is observed that at low-frequency $M'$ is zero due to lack of restoring forces for mobile lithium ions and there is an increase in $M'$ with increase in frequency. $M'$ reaches a maximum value corresponding to $M_\infty$ due to the relaxation process [29]. Similar qualitative behavior is observed for other glass samples of this series.

![Fig. 3. Variation of real part of electric modulus ($M'$).](image)

**Fig. 4** shows the variation of imaginary part of the electric modulus ($M''$) with frequency. From this figure, it is observed that $M''_{\text{Max}}$ shift towards higher frequencies with the increase of temperature. The center of the relaxation peak is characterized by $f_p$ and further used to calculate relaxation time $\tau$ ($\tau = \frac{1}{2\pi f_p}$) by using condition $\omega_c \tau = 1$.

![Fig. 4. Variation of imaginary part of electric modulus ($M''$) with frequency and temperature for PR 3 glass sample.](image)

The calculated value of relaxation time $\tau$ is plotted against $10^3/T$ as shown in **Fig. 5** [25] and it is observed that it follows the relation given by the equation $\tau = \tau_0 \exp\left(\frac{E_{\text{a}}}{k_B T}\right)$. From the slope of fitting lines of **Fig. 5** $E_{\text{a}}(\tau)$ was calculated and depicted in **Table 1**. The similarity in the values of $E_{\text{a}}(\text{dc})$ (**Fig. 1**) and $E_{\text{a}}(\tau)$ confirms the involvement of Li$^+$ ions as a charge carrier in both the relaxation and conduction processes (**Table 1**).

![Fig. 5. Variation of relaxation time with temperature.](image)

To examine the effect of composition and temperature on conduction mechanism scaling is introduced. Normalized plots of conductivity and imaginary part of modulus have been studied using the master plots. **Fig. 6** shows the result of normalized plot where log ($\sigma'/\sigma_{\text{dc}}$) used as the Y-axis parameter and log ($f/\sigma_{\text{dc}} T$) as an X-axis parameter for PR 3 glass samples as a representative [20, 24, 25]. Data is found to be scaled very well on the single master curve for different temperature.

![Fig. 6. Conductivity scaling data of PR 3 glass sample.](image)

The reduced imaginary part of a modulus ($M''/M''_{\text{Max}}$) has been plotted as a function of log ($ff_\infty$) for PR 3 glass sample as a representative is shown in **Fig. 7**. It is observed from this figure that the data also collapses excellently $M''/M''_{\text{Max}}$ versus log ($ff_\infty$)) for all temperatures [25, 29]. This study suggests that the dynamical processes and conduction mechanism is temperature independent [25, 29].
The frequency and temperature dependent study were performed on the 27.5 Li_2O-(72.5-X) B_2O_3-X Pr_2O_3 glass series in the wide range of frequency and temperature. From this study it is confirm that Li^+ ions are the main charge carriers responsible for conduction process. With the addition of Pr^3+ ions in the glass matrix conductivity of glasses decrease. The decrease in conductivity is mainly due to the increase in the rigidity of glass structure. Higher ionic radius and molecular weight of Pr^3+ ions also hinder the movement of Li^+ ions in the glass matrix.

These results are in accordance with Tg results. Performed scaling suggests that during the conduction process and relaxation process, Li^+ ions have to overcome the same potential barrier. The calculated activation energy associated with the dc conductivity and that associated with the relaxation process are very close to each other which proves the involvement of Li^+ ions in conduction as well during relaxation process. Further, the present study proves that the conduction processes in the prepared glasses are compositional dependent and not the temperature dependent. Based on the present study we propose that these glasses can be useful as insulating material after certain modifications in the compositions.

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**Reference**


**Conclusion**

The frequency and temperature dependent study were performed on the 27.5 Li_2O-(72.5-X) B_2O_3-X Pr_2O_3 glass series in the wide range of frequency and temperature. From this study it is confirm that Li^+ ions are the main charge carriers responsible for conduction process. With the addition of Pr^3+ ions in the glass matrix conductivity of glasses decrease. The decrease in conductivity is mainly due to the increase in the rigidity of glass structure. Higher ionic radius and molecular weight of Pr^3+ ions also hinder the movement of Li^+ ions in the glass matrix.