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# Ionic conductivity of praseodymium doped silver-borate glasses

G.V. Jagadeesha Gowda [a], B. Eraiah [b,*], R.V. Anavekar [b]

[a] Department of Physics, Sapthagiri College of Engineering, Bangalore 560057, India
[b] Department of Physics, Bangalore University, Bangalore 560056, India

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ABSTRACT

Glasses of the composition $x\mathrm{Pr_6O_{11}}$–$(35-x)$ $\mathrm{Ag_2O}$–$65\mathrm{B_2O_3}$ ($x$ = 0, 0.1–0.5 mol%) have been prepared using the melt quenching method. The ac and dc conductivity and dielectric properties of glass have been measured over a wide range of frequencies and temperatures. Experimental results indicate that the ac conductivity and the dielectric constants depend on temperature, frequency and praseodymium content. The conductivity as a function of frequency exhibited two components: dc conductivity ($\sigma_{dc}$), and ac conductivity ($\sigma_{ac}$). The activation energies are estimated and discussed. The impedance plot at each temperature appeared as a semicircle passes through the origin. In all the samples, only one semicircle has been observed over the entire range of temperature studied indicating only one type of conduction mechanism.



## 1. Introduction

The ionic conductivity of glasses has attracted considerable attention in recent decades because of their potential applications in solid state batteries, chemical sensors, and smart windows. The use of glasses both as electrolyte and electrode materials has given a boost to the study of ion transport in glasses and search for a new glassy material. Silver borate glasses in particular have attracted a lot of attention because of their high ionic conductivity, especially when mixed with $\mathrm{Ag^+}$ ion. This property makes a basis for their applications in electrochemistry as solid electrolytes [1–5]. The optimization of such properties requires a good knowledge of the microscopic glass structure. In particular, a deeper knowledge of the local environment of the moving ions is highly desirable. Silver Borate glasses are the classical glass forming systems and have been extensively studied in the literatures [2–6]. It is well known that silver ion conducting batteries developed high voltages and high energy density due to their light weight and highly electropositive character of the silver metal [3–5]. These glasses have several advantages over crystalline counterparts, ease of fabrication into complex shapes.

Impedances are complex and from the Cole–Cole plot of these complex quantities, one can extracts not only conductivities but limiting high and low frequency dielectric constants. The same alternate current (ac) conductivity data is often recast to obtain information on dielectric moduli ($M'$ and $M''$) from which relaxation behavior is examined. The conductivity is generally studied as a function of temperature and it may also depend on structural changes in the material. In this point of view it is interesting because the conductivity of vitreous material is caused by at least two different contributions. The first one is thermal activation, the conductivity increases with temperature according to the Arrhenius law [6,7]. The second one is the structural change of the glass with temperature and composition, which also causes a variation of conductivity. Therefore it is also interesting to understand the dynamics of the mobile ions in solid ion conductors by interpreting the frequency dependent features in their dielectric response. Silver borate glasses containing transition metal ions such as manganese, nickel are known to materials for electrodes [8,9]. In the literature we find that these glasses have not been studied extensively. In an effect to understand the conductivity behavior of $\mathrm{Pr_6O_{11}}$–$\mathrm{Ag_2O}$–$\mathrm{B_2O_3}$ glass system has been taken up for the present investigation.

In this paper we report both dc conductivity and ac conductivity and relaxation behavior on $\mathrm{Pr_6O_{11}}$–$\mathrm{Ag_2O}$–$\mathrm{B_2O_3}$ glasses over wide range of compositions, temperatures and frequency.

## 2. Experimental

The glasses with composition $x\mathrm{Pr_6O_{11}}$–$(35-x)$ $\mathrm{Ag_2O}$–$65\mathrm{B_2O_3}$, ($x$ = 0, 0.1–0.5 mol%) have been prepared using high purity anlar grade chemicals Praseodymium oxide ($\mathrm{Pr_6O_{11}}$), Silver oxide ($\mathrm{Ag_2O}$) and Boric acid ($\mathrm{H_3BO_3}$). The nominal composition of the starting mixtures is given in Table 1. The starting materials were weighed in required proportions and components were thoroughly mixed by grinding together and were heated in porcelain crucible at 500 °C for 30 min to get rid of water and $\mathrm{CO_2}$. The batches melted in a crucible at about 1100 °C to get homogeneous melt. The glass samples were obtained by quenching

* Corresponding author. Tel.: +91 94498 04014.
*E-mail address:* eraiah@rediffmail.com (B. Eraiah).

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**Table 1**
Compositions of the glasses along with codes of designation and their corresponding conductivity (at 443 K) $E_{dc}$, $S$ and $\beta$.

| Code | Composition (mol %) | | | $\sigma_{dc}$ ($S\,cm^{-1}$) at 443 K | $E_{dc}$ (eV) | $S$ | $\beta$ |
|---|---|---|---|---|---|---|---|
| | $Pr_6O_{11}$ | $Ag_2O$ | $B_2O_3$ | | | | |
| A1 | 0.0 | 35.0 | 65 | $5.6 \times 10^{-6}$ | 0.47 | 0.42 | 0.65 |
| A2 | 0.1 | 34.9 | 65 | $6.2 \times 10^{-6}$ | 0.43 | 0.47 | 0.62 |
| A3 | 0.2 | 34.8 | 65 | $4.3 \times 10^{-5}$ | 0.40 | 0.48 | 0.63 |
| A4 | 0.3 | 34.7 | 65 | $5.7 \times 10^{-5}$ | 0.36 | 0.40 | 0.67 |
| A5 | 0.4 | 34.6 | 65 | $5.1 \times 10^{-4}$ | 0.34 | 0.45 | 0.64 |
| A6 | 0.5 | 34.5 | 65 | $5.6 \times 10^{-4}$ | 0.31 | 0.41 | 0.60 |

the melt between brass blocks pre-heated at about 100 °C. The glasses suitable for electrical conductivity measurements were obtained. All the samples were annealed below their transition temperature to remove the thermal strains of the sample. The prepared samples were taken in the form of circular disc of diameter of about 1 cm and thickness of about 0.1 cm for electrical relaxation measurements. Before making electrical measurements, the sample surfaces were polished, then coated with silver paste and dried over 6–12 h at 330 K. The electrical measurements were carried out by sandwiching the samples between electrical leads made up of silver.

Precision impendence analyzer [Agilent-4294A] was used to measure the capacitance ($C_p$) and conductance ($G$) in the frequency range from 6 Hz to 10 MHz. Measurements were made in temperature ranges from 343 K to 443 K. A home built cell assembly (2-terminal capacitor configuration and spring loaded silver electrodes) was used for measurements. The sample temperature was measured using a Pt-Rh thermocouple positioned very close to the sample.

### 2.1. Analysis of data

The capacitance ($C_p$) and conductance ($G$) of all the samples were measured over a wide range of composition, frequency and temperature from the impedance analyzer. The $C_p$ and $G$ were used to evaluate the real and imaginary parts of the complex impedance using standard relations [10,11].

$$Z^* = Z' + jZ'' = 1/(G + j\omega C_p) \quad (1)$$

$$Z' = Gd/A \quad (2)$$

$$Z'' = \omega C_p/(G^2 + \omega^2 C_p^2) \quad (3)$$

The dc conductivity ($\sigma_{dc}$) for each sample was estimated using the expression:

$$\sigma_{dc} = Gd/A \quad (4)$$

where $d$ and A are the thickness and area of the sample respectively and ω is the angular frequency.

The real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of the complex dielectric constant were calculated from the relations,

$$\varepsilon' = C_p d/A\varepsilon_o \quad (5)$$

$$\varepsilon'' = \sigma/\varepsilon_o\omega \quad (6)$$

where, $\varepsilon_0$ is the permittivity of the free space.

The data were also analyzed using the electrical modules formalism. The real ($M'$) and imaginary ($M''$) parts of the complex electrical modules ($M^* = 1/\varepsilon^*$) were obtained from $\varepsilon'$ and $\varepsilon''$ values using the relations:

$$M' = \varepsilon'/(\varepsilon'^2 + \varepsilon''^2) \quad (7)$$

$$M'' = \varepsilon''/(\varepsilon'^2 + \varepsilon''^2)$$

## 3. Results and discussion

### 3.1. Dc conductivity

Direct measurement of dc conductivity of the sample is not possible because of the polarization effects at the sample-electrode interface and practical difficulties in finding suitable electrode. These difficulties can be overcome by analyzing ac impedance data using impedance spectroscopy technique. The dc conductance was determined from the semicircular complex impedance ($Z''$ versus $Z'$) plots. The impedance plots for all the samples were found to be good semicircles. Impedance plots for $0.5Pr_6O_{11}$–$34.5Ag_2O$–$65B_2O_3$ glass sample at different temperatures are shown in Fig. 1. In all the samples, only one semicircle has been observed over the entire range of temperature studied indicating only one type of conduction mechanism. The intersection points of the semicircles shifted to lower and lower $Z'$ values with increasing temperature, suggesting that the dc conductivity is a thermally activated process. The dc conductivities were calculated by taking the intersection points of the semicircle on real axis.

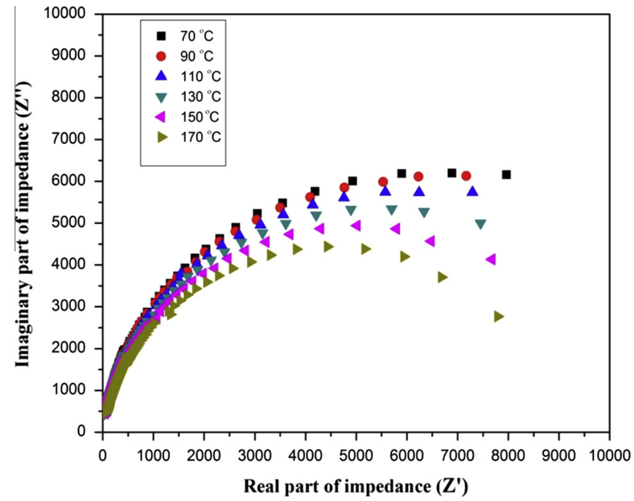


**Fig. 1.** Typical cole–cole plot of $0.5Pr_6O_{11}$–$34.5Ag_2O$–$65B_2O_3$ glass at different temperatures.

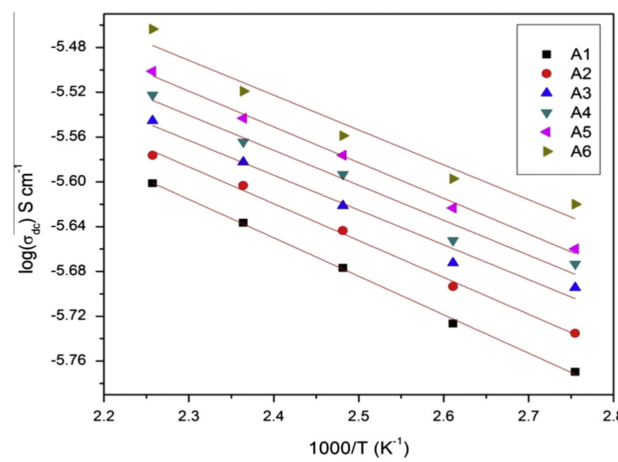


**Fig. 2.** Variation of $\log(\sigma_{dc})$ versus $1000/T$.

The temperature dependence of dc conductivity in the form of $\log(\sigma_{dc})$ versus $1000/T$ plot for some of the samples are shown in Fig. 2. In all the samples, single linear variation of $\log(\sigma_{dc})$ versus $1000/T$ has been observed. It is observed that the dc conductivity increases with increase in temperature and obey the Arrhenius behavior [12,13].

$$\sigma_{dc} = A\exp[-E_{dc}/kT] \quad (8)$$

where $A$ is the pre-exponential factor, $k$ the Boltzmann constant, $E_{dc}$ is the activation energy for the dc conduction. The data of each sample has been least square fitted to straight line to evaluate the activation energy for electrical conduction. The dc activation energies ($E_{dc}$) is calculated from the slopes of the $\log(\sigma_{dc})$ versus $1000/T$ plot for various compositions of the samples. Fig. 3 shows the composition dependence of dc activation energy for the samples. It is observed from Fig. 3, as the concentration of $Pr_6O_{11}$