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Transport Properties of Niobium Doped Silver-Borate Glasses

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Abstract

Objective: To create a broad composition range of Nb_2O_5 doped silver-borate glasses without adding any reducing chemical agents and to achieve ac-dc conduction mechanism. **Methods**: Borate glasses compositions, (1-x)Nb_2O_5-65B_2O-(35-x)Ag_2O, (Where x=0.1 to 0.5 mol%) have been synthesized by conventional melt-quenching technique. Temperature dependent conductivity over a wide range of frequency (40-10MHz) has been performed. **Findings:** Only one semicircle is visible in the impedance plots, suggesting the existence of a single kind of conduction mechanism. Fitting the data to the Almond West type power law behavior, $\sigma(\omega) = \sigma_0 + A\omega^s$ is used for the analysis of the ac conductivity. It is also discovered that the power law exponent "s" rises as the temperature rises. Indicating the temperature dependence of the conductivity of the samples. **Novelty:** The preparation of niobium doped silver-borate glass samples is achieved without the reducing agents and established the wide range of conduction mechanism by both Nb^+ and Ag^+ ions for the first time.

Keywords: Glass; Transport Properties; AC-DC Conductivity; Ag-Ions; Almond-West Power Law

1 Introduction

There is academic and practical interest in ion transport in amorphous materials [1–3]. Solid-State-Ionics (SSI) is a large class of materials whose technologically important feature is the movement of mobile charges (via hopping) through a solid matrix. Both ion conducting crystals and glasses are present in these materials, which are utilized in solid state batteries and chemical sensors, among other technologies. Understanding the nature of ion transport in these materials is also intriguing from an academic standpoint. At normal temperatures, the best Niobium doped conducting glasses can achieve conductivity of up to 10^{-2} S/cm. Glasses containing silver borate are emerging as a prototype vitreous electrolyte system. Although the AgI-doped borates' exceptional ion conducting capabilities have been known for a while, the most recent research focuses on their spectroscopic [4], structural [5], acoustical [6], and thermochemical [7] characteristics. Therefore, knowledge of the structure and ion transport mechanisms of silver borate glasses may aid in the study of other systems of vitreous electrolytes. It has been observed that the properties of silver borate glasses are significantly influenced by the frication technique. These materials are very desirable because of their high ionic conductivity and a variety of applications, such as solid batteries, chemical sensors, electrochromic displays, antibacterial and antimicrobial biomaterials, and biomaterials for the treatment of cancer and HIV. Recently, the reverse Monte Carlo method [8,9], has been used to model the structure of fast ion conducting glass systems using X-ray and neutron-diffraction data of silver borate glasses. This method predicts that the majority of Ag+ ions are coordinated to both I ions and BO_4 units in the network. This article provides a detailed explanation of the investigation and study of the conductivity properties of a special glass system known as niobium doped silver-borate glass.

2 Methodology

Borate glasses compositions, (1-x)Nb_2O_5-65B_2O-(35-x)Ag_2O, (Where x=0.1 to 0.5 mol%) have been synthesized by conventional melt-quenching technique [9,10]. Glass samples of compositions selected for the present investigation are given in Table 1. Appropriate proportions of analytical grade reagents of Ag_2O, B_2O_3 and Nb_2O_5 were thoroughly mixed in an agate mortar and melted in a porcelain crucible at 1150±10°C for about 1 h until a bubble-free liquid was formed. The resultant melt was then cast in a brass mould and subsequently annealed at 100°C to remove thermal stress. The compositions of the glasses investigated in this study are given in Table 1 . The amorphous state of the glasses was checked by the X-ray diffraction method. The final dimensions of the samples used for the electrical measurements have a thickness of 0.1 cm and a diameter of 1 cm. A thin coating of silver paint was applied (to the larger area faces) on either side of the glasses to serve as electrodes for electrical measurements. The instrument used for conductivity measurement is Precision impendence analyzer [Model: Agilent-4294A, Japan] with the frequency range 40 Hz-110 MHz at room temperature and as well as temperatures from 373–473 K with a 10 K temperature step. A home-built cell assembly was used as a sample holder for the measurement of conductivity.

Table 1. Glass composition with codes

Sample Code	Mol (%)		
	Nb_2O_5	B_2O_3	Ag_2O
L1	0.1	65	34.9
L2	0.2	65	34.8
L3	0.3	65	34.7
L4	0.4	65	34.6
L5	0.5	65	34.5

3 Results and Discussion

3.1 DC-Conductivity studies

The electrical conductivity parameters such as capacitance (C_p) and conductance (G) have been measured at various frequencies (w) with the constant input signal voltage. The measured values of C_p and G were used to evaluate the real (Z') and imaginary (Z") parts of the complex impedance using the standard relations [11].

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

$$Z' = \frac{G}{(G^2 + \omega^2 C_p^2)} \quad (2)$$

$$Z'' = \frac{\omega C_p}{(G^2 + \omega^2 C_p^2)} \quad (3)$$

The dc conductance values were determined using the expression,

$$\sigma_{dc} = (1/Z)(d/A) \tag{4}$$

where d and A are the thickness and the area of the sample respectively and Z is the dc resistance obtained from the intersection at the low frequency end of the semicircle with the Z' axis from the semicircular complex impedance (Z' vs Z") plots.

Arrhenius plots of the D.C. conductivities were drawn using the expression

$$\sigma = \sigma_0 exp[-E_{dc}/kT] \tag{5}$$

where σ_0 is the constant called pre-exponential factor, E_{dc} is the dc activation energy, T is the temperature in K and k is Boltzmann's constant. Values of E_{dc} were estimated from the slopes of linear regression analysis of log(σ_{dc}) vs 1000/T plots.

The typical impedance plots (Cole–Cole plots) for glass sample L4 is shown in Figure 1 . All the investigated glass samples show only one semicircle, indicating only one type of conduction (i.e., ionic) mechanism.

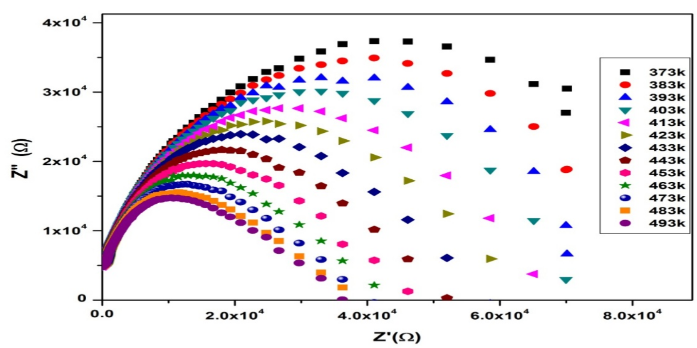

Fig 1. Typical combined plots of Z' Vs Z" for L4 glass

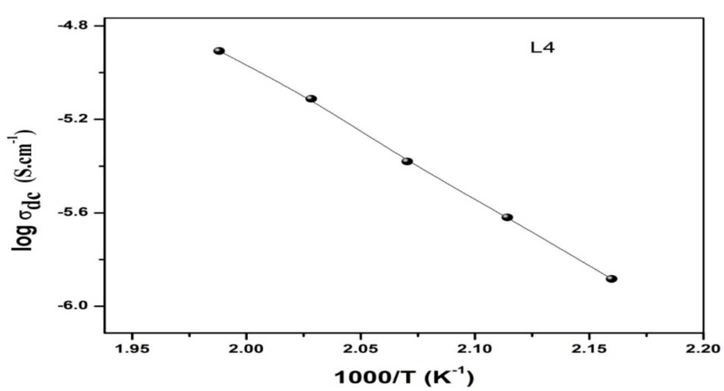

Fig 2. Typical variation of log ($\sigma_{d.c}$.) versus (1000/T) for L4 glass

Over the whole temperature range, the dc conductivity for different compositions plotted as a function of 1000/T exhibits Arrhenius behavior, as seen in Figure 2. The activation energy (with an error $\pm$ 0.03) for electrical conduction has been calculated by fitting each sample's data using least squares to a straight line. The dc activation energies (E_{dc}) numerical data were obtained from log (σ_{dc}) against (1000/T) graphs. Activation energies range between 0.4 and 0.5 eV. Because of the improvement in the silver-borate network with the addition of Nb ions, the observed variance in conductivity is complemented by the rise in activation energies [12,13].

3.2 AC conductivity studies

The ac conductivity s(w) for each sample in the frequency range of ~100 Hz to 10MHz between 373K and 473K was estimated using the expression

$$\sigma = G\left(\frac{d}{A}\right) \tag{6}$$

where d and A are the thickness and area of the sample respectively. This frequency dependent behavior of conductivity is analyzed on the basis of Jonscher's universal power law which is also called the Almond-West type of power law with a single power exponent [10–13].

$$\sigma(\omega) = \sigma_0 + A\omega^s \tag{7}$$

where σ_o is frequency independent and it is identified with the dc conductivity and the second term is the purely dispersive component of the ac conductivity depending on the angular frequency w(=2pf) of the applied field, 'A' is a constant for a particular temperature and 's' is the power law exponent in the range 0 < s < 1.

Figure 3 displays a typical logarithmic curve of L4 glass's ac conductivity as a function of frequency. The standard computer matched conductivity data to Equation (1), as seen in Figure 3 (solid lines). Since the quality of fit was found to be satisfactory in every case, a single exponent fit appeared to be adequate. The values of $\sigma_0$obtained from the Almond–West type power law fit and the dc conductivities (σ_{dc}) obtained from the impedance plots are similar in magnitude. The frequency dependence of the conductivity for a typical glass composition at different temperatures is shown in Figure 4.

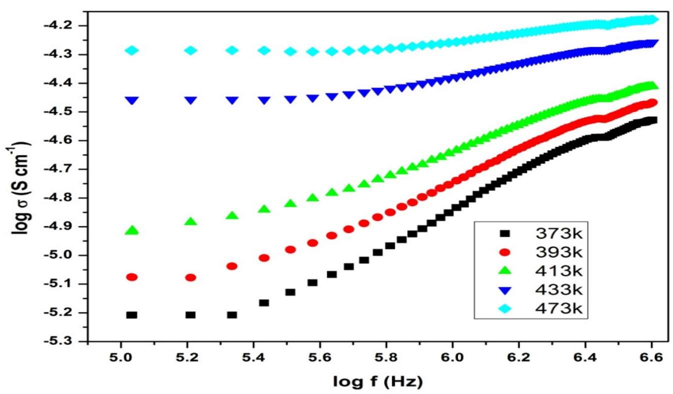

Fig 3. Typical Plots of log (σ) versus log (f) for L4 glass at different temperatures

Frequency functions as a pumping force that pushes the charge carriers from one conduction state to another, particularly at low frequencies, the rise in A.C. conductivity with increasing frequency is a desirable outcome. The most common conduction mechanism in Ag-substituted glasses involves electron hopping between ions with differing valences in equivalent lattice positions. This behavior is the overall tendency of these glasses. Additionally, this outcome is consistent with other writers' findings [5,14].

The conductivity at low frequencies is unaffected by the frequency at which the dc conductivity occurs. As the temperature rises, the frequency dispersion begins at a higher frequency. The relevant plots are shown in Figure 4. Temperature and frequency have a significant impact on the total conductivity σ_{tot}, which displays the characteristic hallmarks of an ionic conductor. Because of the shallow traps, it is seen that the overall conductivity of the glass samples is almost constant at lower frequencies, while at higher frequencies, it follows a power relation [5,15].

Further, at low frequencies, a frequency independent conductivity that characterizes the D.C. conductivity is produced by the random diffusion of the ionic charge carriers by activated hopping. σ_{tot} shows dispersion at higher frequencies, rising power-law-like with increasing frequency. As the temperature rises, the D.C. to A.C. conductivity transition area moves to higher frequencies. This change may be due to thermally generated charge carriers at high temperatures. These results are well matched with the reports on Ag ion conductivity glass samples [5,14–16]. The measured frequency-dependent conductivity is described by Equation (7). The conductivity behavior in these glasses is attributed to the additional lattice vacancies caused by disorder and is an intrinsic feature of this structure, as would be the case in a conventional ionic conductor. This significantly facilitates ionic mobility [15–17].

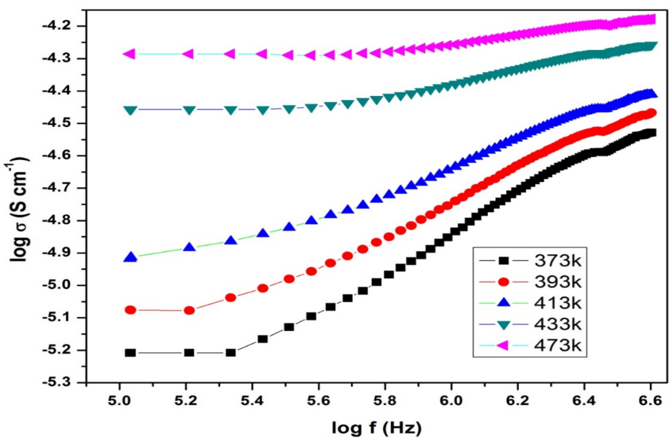

Fig 4. Typical Plots of ac conductivity data fitted to single power law equation for L4 glass at different temperatures

The impact of Ag ions on the conductivity of the Zinc Selenium Phosphate Glass System across a broad temperature range was investigated by Reddy GNK et al [15]. A transition from a normally electronic (polaronic) conductive state is confirmed by the acquired data. A deep minimum in electrical conductivity around three orders of magnitude is what defines this transition. The logic goes as follows: oppositely charged Ag ions are drawn to mobile electrons or polarons created when a V(IV) atom captures a moving electron. As a neutral entity, this so-formed cation–polaron pair likes to move together. Therefore, this activity does not contribute to electrical conductivity since there is no net displacement of charge involved in the movement of these pairs. There are two types of independent migrating paths, in which one type of path involves an electronic transfer in the chain (IV)V and (V), while the other type is created by the regular position of nonbridging oxygen along the network-former chains that permits the ion displacement. Consequently, the addition of Ag_2O inhibits the electronic current by gradually closing the electronic channels [15,16]. The difference in the AC conductivity of silver ate with niobium glasses as a function of the silver concentration can be explained by these two hypotheses. The electronic conductivity decreases when the network modifier Ag_2O mol% increases because the electronic pathways become increasingly clogged. The active centers for ionic conduction, which are primarily made up of non-bridging oxygen, get closer as the Ag_2O content rises, and ionic (cationic) transport begins and gradually increases. The shift in the mechanism of the electrical transport process in these glasses with the variation of Ag_2O is thus reflected in the relative minimum in the AC conductivity. This result is well matched with the Ag^+ ion conducting mechanism seen in the reported glass AgI-Ag_2O-MoO_3 [17].

The values of power law exponent 's' are listed in Table 2. The 's' values are found to be almost constant and lie between 0.3 and 0.6. Significantly lower than unity and are essentially temperature independent. It increases comparatively more steeply with temperature than β, the exponent in the KWW (Kohlrausch-Williams-Watts) expression. Hence these results are well in agreement with the other reports on the conductivity studies [16,17].

Table 2. Temperature, σ_{dc}, β, s and activation energy (E_{dc}) for L4 glass

Temperature (K)	σ_{dc} (S/cm)	β	s	E_{dc} (eV)
373	2.53906×10^{-5}	0.38	0.3788	0.35
393	6.69019×10^{-5}	0.41	0.3186	0.39
413	7.97087×10^{-5}	0.46	0.3021	0.37
433	2.26190×10^{-6}	0.43	0.4848	0.45
453	1.18220×10^{-6}	0.40	0.5242	0.47
473	1.57522×10^{-7}	0.36	0.6245	0.49

4 Conclusion

The effect of Niobium on the silver-borate glass system was investigated in an attempt to see the enhancement of ionic conductivity. This electrical conductivity displays the characteristics of ionic conductors and varies significantly with temperature and frequency. It appears that the power law exponents' fluctuation with temperature is independent. The stretched exponential relaxation function has been used to assess the dielectric relaxation data. It is discovered that the stretched exponent β is not affected by composition or temperature. Additionally, the scaling of the modulus and ac conductivity data demonstrates a good coalescence into a single master curve, suggesting that the conduction mechanism is unaltered and that there is a good time-temperature superposition. The D.C. conductivity is characterized by a frequency independent conductivity that arises from the random dispersion of the ionic charge carriers by activated hopping at low frequencies. As the temperature rises, the D.C. to A.C. conductivity transition area moves to higher frequencies. This change may be due to thermally generated charge carriers at high temperatures. Higher frequencies show dispersion in electrical conductivity, which raises power-law with frequency. The addition of Nb in the silver-borate glasses enhances the conduction compared to the conduction mechanism in similar glasses containing only Ag+ ions as seen in the earlier reports.

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