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Complex Impedance Spectroscopy Analysis of Quaternary Ionic Glass system

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An investigation uses the rapid quench method to prepare and characterise a quaternary glass system with the chemical composition $MI - M_2O - B_2O_3 - P_2O_5$. Alkali metal ion (M), metal oxides (M_2O), boron oxide (B_2O_3), and phosphorus oxide (P_2O_5) make up the composition of the glass system. This points to a complicated network in which alkali metal oxides alter the network structure and phosphorus and boron serve as mixed network formers.
The rapid quench approach was used to prepare the glasses, which usually entails rapidly cooling a molten material to inhibit crystallisation and encourage the creation of an amorphous (glassy) structure. X-ray diffraction (XRD) was utilised for structural characterisation to analyse the degree of crystallinity.

Keywords: Glass former & modifier, Additive halide, Continuous Random Network (CRN), Rapid quenching/cooling, degree of crystallinity, Temperature and Frequency Dependent Conductivity, Power Law Behaviour, Ionic conductivity.

1. Introduction

The phenomenon known as fast ion conduction occurs when some solid materials have incredibly high ionic conductivity. Superionic conductors also defined as fast ion conductors, exhibit this behaviour [1]. When ions in a solid material move quickly through the network, this is known as fast ion conduction. The continuous random structure, defects, or interstitial sites, which offer ion movement channels, make this possible [2]–[5]. Several ceramics, glasses, and polymer electrolytes are common fast ion conductors. Glasses possess a disordered structure because they lack long-range crystalline order [6]. In contrast to a crystalline counterpart [7], the ion migration is constrained by fixed lattice sites. The disorder in the vitreous produces pathways or channels that allow ions to move more freely. Ionic glasses are amorphous solids formed by rapidly cooling an ion-containing melt. The absence of long-range order in such substances allows the rapid movement of ions. Ion migration for conduction in glasses is primarily due to ion mobility within the disordered structure. The type of ions, the glass composition, and the temperature all influence conductivity. Ionic glasses typically contain alkali metals (Na^+, Li^+, K^+), alkaline earth metals (Mg^{2+}, Ca^{2+}), and other cations. The flexible glass network and the availability of interstitial sites enable ions to hop between nearby sites, which is the primary mechanism of ion transport in glasses. High ionic conductivity depends on the concentration of mobile ions and the capability of the glass network to permit their migration. They make efficient ion transport possible, which is essential to the functionality of these devices. Ionic conductivity can be highly impacted by the type and amount of mobile ions and network formers (like SiO_2 and B_2O_3) in the glass matrix. At higher temperatures, ionic conductivity typically rises with temperature due to increased ion mobility.

By improving the conditions for ion migration, specific dopants can raise ionic conductivity, such as ensuring the long-term stability and durability of ionic glasses in real-world applications by improving ion mobility and conductivity. Researchers are working to optimise the composition and structure of glasses. The need for advanced materials in energy storage and other high-tech applications has kept researchers focused on studying fast ion conduction in ionic glasses. The behaviour of the sodium cations in the competitive glass network structure is one of the fascinating fields of study. Sodium ions modify the overall properties and behaviour of glassy material by interacting with oxygen atoms and other ions in the surrounding network [8]. Our research, which focuses on sodium cation behaviour within the competitive network of the glass structure, can help us gain a fundamental understanding of ion dynamics in amorphous materials, which could have implications for various technologies.

Sodium Borophosphate glass ($Na_2O- B_2O_3- P_2O_5$) is a type of quaternary glass system that consists of sodium oxide (Na_2O), boron oxide (B_2O_3), and phosphorus oxide (P_2O_5) [9]–[11]. This glass system is interesting due to its potential applications in various fields such as optoelectronics, solid-state ionics, and biomaterials [12]. The addition of halides to this system has been studied to understand its effect on the glass network structure and properties. The complex Impedance Spectroscopy (CIS) technique has been employed to elucidate the behaviour of cations in the glass system, providing insights into the electrical properties. The influence of additive halides on the variation in the given parent system allows for an analysis of the glass system. It is interesting to see how the addition of halides affects the overall behaviour and properties of the glass network structure. Hence, the study investigates the role of additives, the structural configuration, and the degree of crystallinity in this glass system, with potential implications for a wide range of practical applications, such as solid-state batteries, fuel cells, and sensors, fast ion conductors are crucial [13], [14].

2. Experimental:

(A) Materials used

Raw materials such as boric acid (H_3BO_3), ammonium dihydrogen phosphate ($ADP - NH_4H_2PO_4$), sodium oxide (Na_2O) and sodium iodide (NaI) were used for the preparation of electrolyte materials.

(B) PREPARATION METHOD FOR GLASS ELECTROLYTE

Glass electrolyte samples were prepared using a carefully mixed chemical mixture, heated, and melted at high temperatures, followed by rapid cooling. Table 1 lists the solid electrolyte samples with varying concentrations of an additive while maintaining a consistent glass composition.

Table 1: Sodium borophosphate glass: Physical parameters

Sodiu	(wt.%)			ρ (/cc	V (c m	OPD ( )
1	69.3	29.7	1	2.48885	52.2136	61.4322
2.5	68.25	29.25	2.5	2.4818	52.3232	60.3746
4	67.2	28.8	4	2.4790	52.5063	59.2385
5	66.5	28.5	5	2.4739	52.6986	58.4075

Physical Characterization:

The Archimedes principle was utilised to measure the density of each glass sample, and the resulting data, including molar volume and oxygen packing density, were derived from density measurements, as given in Table 1 [15]. These findings serve as a testament to the potential for innovation and advancement in our understanding of glass structures and properties.

Structural Characterization:

Based on existing literature, the addition of salt to a system has been shown to enhance its amorphous nature and enable the presence of mobile ions. The XRD pattern, Fig. 1, demonstrates broad and diffused humps at lower angle till 50^0 which progressively broaden with increasing salt concentration, indicating a rise in the full width at half maximum (FWHM) of the peak. This signifies that the system becomes increasingly amorphous as the salt concentration rises.

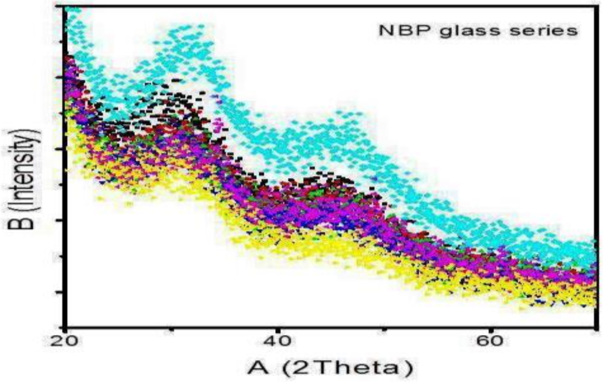

Figure 1: XRD pattern for Sodium Borophosphate glasses.

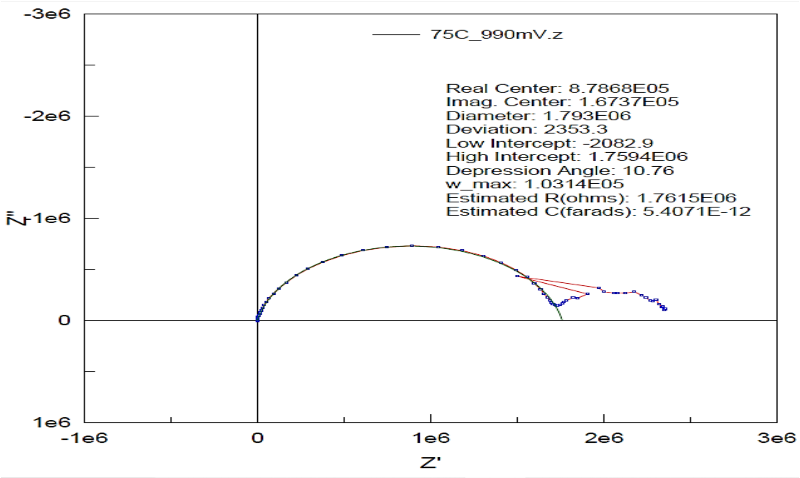

Figure 2: Z' vs Z" plot for Sodium Borophosphate glasses.

Complex Impedance Spectroscopy:

The impedance spectra of the present glass samples were analysed as the amount of sodium iodide is increased in the host glass system, sodium oxide modified borophosphate glass framework. The impedance plots for all NBP series compositions were measured over a temperature and a set of frequency ranges. In the high-frequency regime, a small semicircle appeared due to net ion displacement and the relaxation of mobile ions, indicating long-range ion migration. A larger semicircle was observed in the lower-frequency region, indicating virtually immobile ions due to their inertia [16]. The semi-circular arc represents bulk conduction, while the spur results from the polarization of the electrode as shown in Fig.2. At high temperatures, the appearance of a spike in the impedance plot is consistent with ion mobility being thermally stimulated [16], [17].

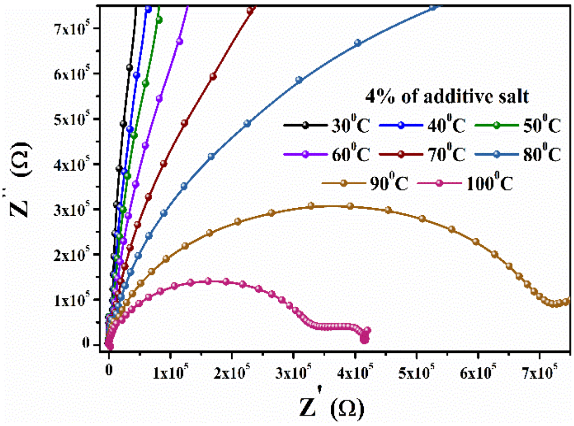

Figure 3: For 4% of additive salt, plot of real and imaginary part of impedance for various temperature.

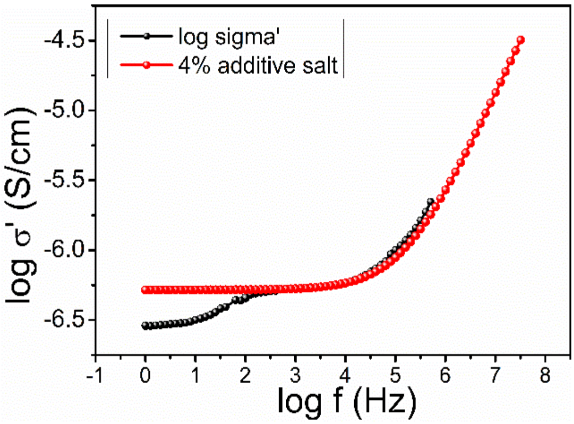

Figure 4: Conductivity plot fitting for 4% of Additive halide in Sodium Borophosphate glass.

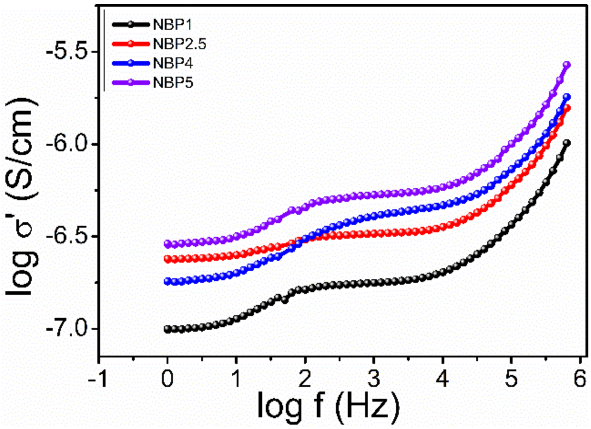

Figure 5: Frequency dependent conductivity for the varying concentration of additive halide in glass samples.

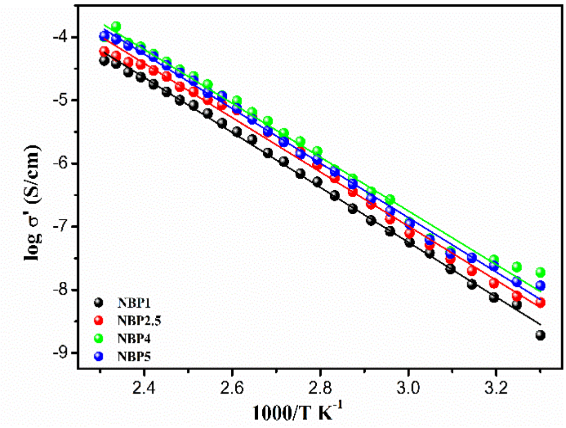

Figure 6: AC Conductivity as a function of the inverse of temperature for the salt concentrations in glass structure.

Additionally, the Z' vs Z'' plot and the equivalent circuit for the glass samples at different temperatures were analysed, and the bulk resistance of the specimen (R_b) was determined using the intercept of an arc with the real axis (Z') as seen in Fig. 3.

Furthermore, in Fig. 4, the impedance spectra can be further analysed by fitting the curve using power law formulation and yields the ac conductivity [18], [19]. Not only the temperature-dependent conductivity but also frequency-dependent conductivity also varies with the variation of halide salt in the parent glass structure as depicted in Fig. 5.

Fig. 6 illustrates a trend wherein the AC conductivity of modified glass rises as the amount of added salt increases [4], [5]. The ions that the additional salts (or dopants) introduce into the glass network can function as charge carriers, changing the overall electrical characteristics of the sample. Since salt facilitates the concentration of ions in the vitreous structure of glass, it can affect the material conductivity by facilitating the movement of charge carriers, such as electrons or ions. The glass, on the other hand, is typically an insulator; however, the presence of salt alters its electrical properties [20]–[22]. The ions in the salt can migrate under an applied AC electric field, increasing the ability of the material to conduct electricity. Higher salt concentrations indicate that more ions are available to transport the charge, which can move in response to an applied AC electric field. In an alternating current electrical field, these ions can respond to changing voltage over time, resulting in better conductivity than the basic glass material, Fig. 7.

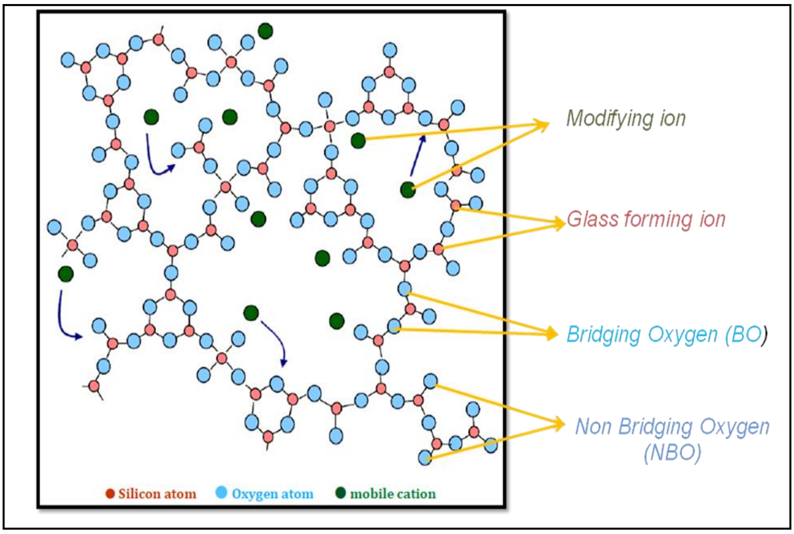

Figure 7: Mixed glass former network doped with additive halide.

3. Conclusion:

In the present study, glassy samples of borophosphate quaternary glass, modified with additive salt and oxide and prepared by a rapid melt quench method, show a significant increase in ionic conductivity with the addition of salt. The maximum ionic conductivity achieved is approximately $\sim 10^8$ S/cm at room temperature. Conductivity analysis indicates that the power law formulation is perfectly obeyed by the vitreous system, and the temperature and frequency-dependent conductivity can be derived from this behaviour.

Overall, the study demonstrates how the AC conductivity of a modified glass structure is affected by the amount of salt added, illustrating the relationship between salt concentration and electrical conductivity in such materials. This relationship is crucial for various applications, including the development of ion-conducting materials for batteries, sensors, and other electronic devices. Understanding this relationship between salt concentration and AC conductivity is essential for designing and optimizing materials for various applications. In fields like solid-state electronics, battery technology, or sensor development, controlling the amount of salt added can be critical for achieving desired electrical performance characteristics. This study highlights the influence of ion introduction on the electrical properties of the material, emphasizing its importance in materials science.

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