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Influence of NaF on the ionic conductivity of sodium aluminophosphate glass electrolytes

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ABSTRACT

This work elucidated the influence of NaF on the structure and ion conductivity of Na_2O-Al_2O_3-P_2O_5-Nb_2O_5 (F-0) glass. The enhancement in ionic conductivity of F-0 glass due to the individual NaF substitution for equal mol% of Na_2O, Al_2O_3 and P_2O_5 have been thoroughly studied. Irrespective of the substitution for any oxides, the addition of NaF increased the concentration of $Al(O,F)_6$ and isolated the PO_4^{3-} tetrahedral units. Impedance analysis has shown that the substitution of NaF for Al_2O_3 has lowered the activation energy and improved the ionic conductivity significantly, which demonstrates this glass composition to be a promising material for solid state sodium ion batteries.

1. Introduction

The trending sodium-ion batteries can be considered more reliable than the persistent Li-ion batteries if they can overcome their drawback of low theoretical energy density owing to higher atomic weight. Moreover, the ever-increasing production cost of Li-ion batteries due to the scarcity of lithium sources in nature also alarms to identify the suitable analogs of batteries. The demand for solid electrolyte as an alternative to the liquid electrolyte materials is growing day by day since it can diminish the flammability, volatility and leakage issues [1]. Nevertheless, glass-based solid electrolytes are considered to be the best choice among the various solid electrolytes (polymers, crystals, ceramics, etc.). The absence of voids in the glass materials is a key advantage which makes them suitable to be used as electrolyte materials. These voids usually restrict the ion migration in ceramic materials [2]. Meanwhile, the appropriate substitution of alkali fluorides for the oxide components in lithium alumina phosphate glasses increases their ionic conductivity [3]. This is mainly attributed to the depolymerization of network structure that intensify the diffusivity of mobile cations. The substitution of alkali fluorides is also known to reduce the molar mass of the compound, thus increasing the overall theoretical capacity of the battery [4]. Detailed composition-structure-property correlating analysis for glasses revealed that the substitution of the cations with other cation in the network structure is one of the most appropriate roots for enhancing or optimizing the performance of the glass materials [5]. However, it is considerably difficult to identify the particular substitution of alkali fluorides for the oxides in multi-component phosphate glasses due to their complex nature of network structure. In the present study, an attempt has been made to identify the effective influence of NaF on the conductivity of $37.5Na_2O$-$22.5Al_2O_3$-$37.5P_2O_5$-$2.5Nb_2O_5$ (mol%) (F-0) glasses by substituting 2.5 mol% of NaF for each equimolar oxide component (Na_2O, Al_2O_3 and P_2O_5).

2. Experimental

A comprehensive synthesis procedure of the glasses was clearly mentioned elsewhere [2]. The detailed composition (in mol%) of the prepared glasses and their classification is given in Table 1. Raman spectroscopy for all the bulk glasses was conducted using Horiba LaBRam HR Evolution Raman spectrometer under 488 nm Ar ion laser of 20 mW power. The impedance spectroscopy

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Table 1
Glass compositions and electrical properties of glasses.

Sample	Concentration (mol%)					Conductivity (Scm^{-1})		Activation energy (eV)
	Na_2O	Al_2O_3	P_2O_5	Nb_2O_5	NaF	at 100 °C	at 200 °C	
F-0	37.5	22.5	37.5	2.5	–	1.58×10^{-8}	1.76×10^{-6}	0.616 ± 0.056
F-Na	35	22.5	37.5	2.5	2.5	1.92×10^{-8}	1.23×10^{-6}	0.588 ± 0.045
F-Al	37.5	20	37.5	2.5	2.5	4.16×10^{-8}	1.84×10^{-6}	0.574 ± 0.043
F-P	37.5	22.5	35	2.5	2.5	2.89×10^{-8}	1.53×10^{-6}	0.590 ± 0.030

technique was utilised to measure the conductivity of the glasses in the temperature range of 50–200 °C under ambient air using Hioki 3532-50 LCR Hi-tester. The detailed experimental conditions during the Raman and impedance measurements were reported elsewhere [2]. The raw impedance data was analysed using the ZView impedance software (Scribner Associates) [6].

3. Results and discussion

The Raman spectra of all the glasses are shown in Fig. 1. It is worth to indicate that the Raman spectrum obtained for F-0 glass, except the strong peak observed at 890 cm^{-1}, is similar to that of previously reported $37.5Na_2O$-$25Al_2O_3$-$37.5P_2O_5$ (mol%) (NAP) glass [2]. The Raman band observed at 1040 cm^{-1} can be ascribed to the symmetric stretching vibrations of $AlPO_4$ units in which phosphorus tetrahedral units are surrounded by AlO_4 tetrahedral units. Considering the vibrations of Nb_2O_5 with Nb in +5 oxidation states and its variable coordination [7], the vibrational band at 890 cm^{-1} can be attributed to the edge-sharing octahedrally coordinated NbO_6 units. Nevertheless, the position of Raman band corresponding to $AlPO_4$ units is the same for both the NAP and F-0 glasses, confirming that the $AlPO_4$ structural units in NAP glass are not much disturbed with the addition of Nb_2O_5. This indicates that the Nb^{5+} ions in the form of NbO_6 units are playing the role of interlinks to connect the distributed $AlPO_4$ units in the network structure of F-0 glass. This is corroborated with the higher value of T_g (474 °C) for F-0 glass (Fig. S1) as compared to that of NAP glass (T_g ~ 416 °C) [8]. The peaks observed at 500 cm^{-1} and 577 cm^{-1} for F-0 glass are attributed to the symmetric stretching vibrations of AlO_6 units and bending vibrations of PO_4^{3-} tetrahedral units, respectively [9]. The peak observed at 430 cm^{-1} is attributed to the bending vibrations of O-P-O bonds in PO_4^{3-} tetrahedral units [9]. It is reported that the incorporation of fluorine atoms into aluminophosphate glasses leads to the formation of mixed $Al(O,F)_6$ units and subsequently, increases the concentration of six-coordinated alumina [10]. The increase in 500 cm^{-1} and 577 cm^{-1} peak intensities due to the substitution of NaF for any oxide component in F-0 glass clearly suggests the increment of $Al(O,F)_6$ and PO_4^{3-} tetrahedral units. This results in a redistribution of sodium cations within the network structure of glasses, which affects the total ionic conductivity of glasses.

Fig. 2 shows the comparative impedance spectra for all the studied glass compositions that were recorded at 373 K. At the temperature below 100 °C, the impedance spectrum contains only one semicircle (with a short tail) mainly related to the bulk conductivity of the glass. Above 125 °C, two semicircles were appeared at high and low frequencies, respectively. The high and low frequency semicircles could be attributed to bulk and inter regional inhomogeneity in glass composition at high temperatures [11]. An equivalent circuit (R1CPE1) (CPE2) at ≤373 K and (R1CPE1) (R2CPE2) at above ≥398 K, where R and CPE stands for resistor and constant phase element, was used to fit the impedance data to extract the resistance and capacitance values. The capacitance values of all the measured glass samples were found to be in the range of ~10^{-11}-10^{-12} Fcm^{-2} for high frequency semicircle and ~10^{-9} Fcm^{-2} for low frequency semicircle indicating that they could be related to the bulk conduction and macroscopic inhomogeneity region in glasses, respectively.

The total ionic conductivity of glasses have been calculated using the formula σ = L/(RA), where L is the thickness of the sample, R is the total resistance and A is the area of cross section. Fig. 3 shows the Arrhenius plot of total conductivity, i.e., log σT vs.

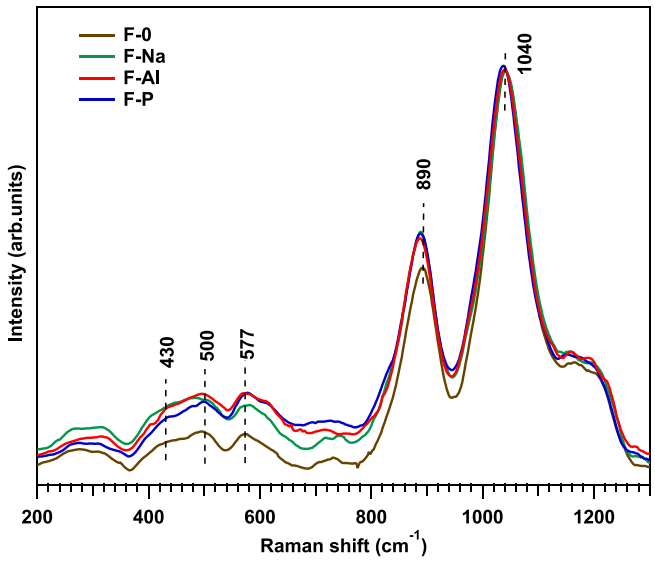

Fig. 1. Raman spectra of as-synthesized glasses.

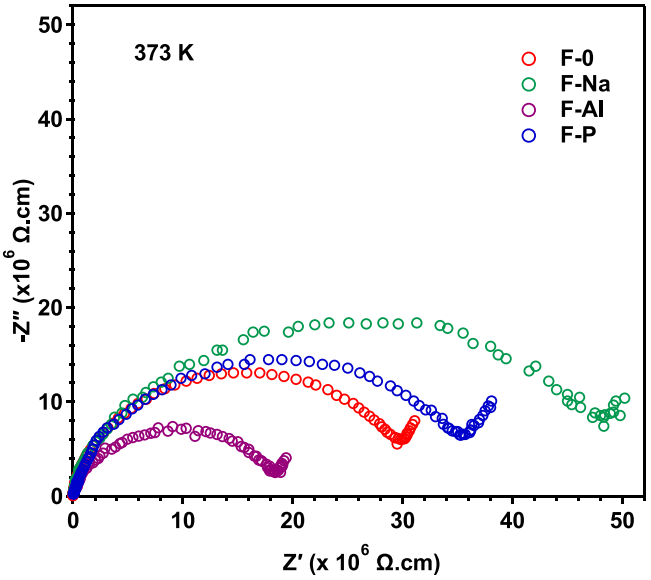

Fig. 2. Electrochemical Impedance spectra (EIS) of the glass samples at 373 K.

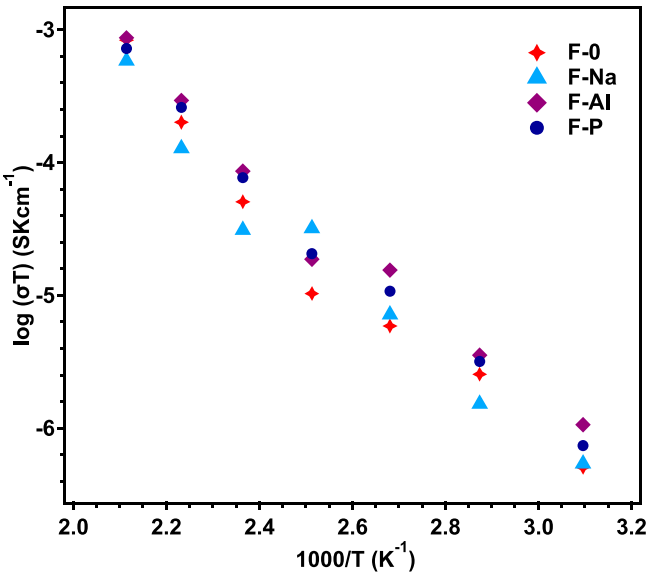

Fig. 3. The temperature dependence of total conductivity of as-synthesized glasses.

1000/T for all the glasses, which exhibit the conductivity values of 10^{-6}–10^{-8} Scm^{-1} in the temperature range of 200–50 °C. The sample F-Al is showing best conductivity among all the studied glasses (Table 1). A profound effect of NaF is clearly visible in F-0 glass since it does not contain any NaF and shows lower conductivity than NaF added glasses. However, slightly improved conductivity is observed with the addition of NaF at ≤100 °C but the same trend does not appear at higher temperatures in these glasses. The activation energy (E_a) of all the samples is found to be in the range of 0.616–0.590 eV in the temperature range of 200–50 °C, as shown in Table 1. The obtained E_a values are comparable to those of the oxide glasses, in which ionic conductivity is known to dominate [12]. However, some minor contribution from electron charge carriers might also be present and cannot be ruled out in the present glass materials. The lowest activation energy of 0.574 eV ± 0.043 eV is found in F-Al sample, which is in line with the highest conductivity among all the studied glass compositions in current work. This improvement might be due to the availability of Na^+ ions for better conduction, through the formation of $Al(O,F)_6$ units and PO_4^{3-} units, by the addition of NaF. A detailed study for this low activation energy, its conduction mechanism, transport properties and high conductivity of F-Al sample is underway and out of the scope of current work.

4. Conclusions

The structural and conductivity variations with the substitution of NaF for Na_2O, Al_2O_3 and P_2O_5 in F-0 glass composition were assessed. F-0 glass network structure was built with $AlPO_4$ structural units followed by their interlinking through the edge sharing NbO_6 octahedral units. The addition of NaF into the F-0 glass was mainly influenced the formation of AlO_6 and PO_4^{3-} units, and enhanced the concentration of ionic charge species with the substitution of NaF for Al_2O_3. The present study clearly suggests that the increase in the concentration of $Al(O,F)_6$ units along with PO_4^{3-} units significantly improved the ionic conductivity of glasses. Thus, in general, concludes that the substitution of NaF for Al_2O_3 is the most appropriate glass composition to enhance the conductivity of F-0 glass.

CRediT authorship contribution statement

Shweta R. Keshri: Methodology, Formal analysis, Investigation, Writing - original draft, Visualization. **Vaijanath V. Bodewad:** Methodology, Formal analysis, Investigation. **Aniket A. Jagtap:** Methodology, Formal analysis, Investigation. **Narendar Nasani:** Conceptualization, Methodology, Investigation, Validation, Writing - review & editing. **Sathravada Balaji:** Methodology, Investigation, Validation, Writing - review & editing. **K. Annapurna:** Methodology, Formal analysis, Investigation, Writing - review & editing, Supervision. **Amarnath R. Allu:** Conceptualization, Methodology, Resources, Formal analysis, Investigation, Writing - original draft, Visualization, Project administration, Funding acquisition, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2020.127763.

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