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# Preparation and electrical conductivity of NaF-$Li_2O$-$WO_3$-$P_2O_5$ glasses

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Several studies have been reported on lithium phosphate glasses to which lithium halides and lithium sulphate have been added. However, there has been no experimental results for the introduction of sodium fluoride into the lithium tungsten phosphate network. How specifically this feature – mixed alkali in the presence of fluorine ion – influences ion transport in the glasses is unclear. This work concerns the investigation of ion transport behaviour of NaF containing lithium tungsten phosphate glasses in order to understand better the role of NaF in the ionic cation transport. Glasses obtained in the system $0.5[x(2NaF)\text{-}(1\text{-}x)Li_2O]\text{-}0.5[0.25(WO_3)_2\text{-}0.75P_2O_5]$ were investigated. The glass samples have been characterised using powder X-ray diffraction (XRD), thermal analysis, density and impedance spectroscopy. X-ray diffraction and thermal studies have confirmed that these glasses can be formed in the range x = 0 to 1. The mixed alkali glasses have shown higher activation energies and lower conductivities compared to single alkali doped glasses and this has been attributed to a mixed alkali influence on the electrical conduction in these systems.

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## 1. Introduction

The need for electrolytes suitable for energy storage has spurred investigations into a number of lithium, silver and sodium ion conducting inorganic glass systems. It is apparent that two strategies have been used in the design of ion conducting electrolytes. The first is to use a combination of two anionic species which has been known to give increased ionic conductivity and is attributed to the so-called mixed-anion effect. The second strategy is to dissolve ionic cation salt in a conventional polymeric silicate, borate or phosphate glass containing a same cation. The increased conductivity is attributed to a volume increasing effect of the dissolved ionic salt. In this context, phosphate glasses containing $Li^+$ as conducting ions are considered to be solid electrolytes [1]. At room temperature the dc conductivity is in the range $10^{-8}$ - $10^{-6}$ ($\Omega^{-1}.cm^{-1}$) and it increases by as much as a factor of $10^5$ at temperatures near the glass transition. The structure of phosphate glasses has the ability to accept a wide range of ionic substitution without altering structure, often accompanied by an increase of electroconductivity [2-4].

Recently [7-10], it is reported that conductivity anomalies could exist in transition metal (TM) oxide containing alkali phosphate glasses. Such anomaly is associated with the fact that the negatively charged polarons (effectively the d-electron located on a TM centre) interact with mobile cations (alkali) to form uncharged diffusing entities minimizing the conductivity. Such reduction of the conductivity is associated with the so-called "ion–polaron effect" (IPE) [7]. More recently, Abbas et al. [11] and Bih et al. [12 ] by selecting adequate glass compositions in the systems $Li_20\text{-}Na_2O\text{-}MoO_3\text{-}P_2O_5$ and $Li_20\text{-}Na_2O\text{-}WO_3\text{-}P_2O_5$, respectively, have studied the mixed alkali effect (MAE) without interference with IPE effect.

The main aim of this paper is to assess the electric and thermal properties of $0.5[x(2NaF)\text{-}(1\text{-}x)Li_2O]\text{-}0.5[0.25(WO_3)_2\text{-}0.75P_2O_5]$ glasses at high alkali compositions, with the view for stabilization of tungsten in the high valency state $W^{6+}$, and examine how different compositions affect these properties. This set of glasses is characterized by: (i) a tungsten/phosphorus constant ratio and (ii) the total concentration of alkali cation very high as 50 mol%.

## 2. Experimental

The samples of lithium and sodium tungsten-phosphate glasses were prepared from appropriate mixtures of reagent-grade $Li_2CO_3$, NaF, $WO_3$ and $NH_4H_2PO_4$. In order to prevent the excess boiling and consequent spillage, water and ammonia in $NH_4H_2PO_4$ were removed initially by preheating the mixture at 300 °C for about 12h. The resulting mixture was then melted for a while at 850-1000 °C, depending on the compositions. Finally, they were quenched to room temperature in air.

All prepared glasses have been first characterised by means of X-ray diffraction (XRD), using a Seifert XRD 3000 instrument, in order to verify the vitreous character (or crystalline) of the elaborated samples. Differential Thermal Analysis (DTA) was performed using a Seiko DTA apparatus under nitrogen atmosphere with a heating rate of 10°C/min. The density of the samples was determined using Archimedes method with diethyl orthophtalate as the displacing medium.

For measurements of electrical conductivity, silver electrodes were applied onto two opposite sides of the samples. The electrical conductivity was determined from the impedance /admittance spectroscopic method. The spectra were carried out on a Hewlett Packard Model 4284A precision LCR Meter in the frequency range 10 Hz to 1 MHz with temperatures changing from 20 to 260°C.

## 3. Results

The elaborated samples were subjected to X-ray diffraction studies. All as-prepared materials show a broad diffraction halo in the X-ray diffraction patterns which are typical of amorphous structures. The obtained glasses in the 0.5(x(2NaF)-(1-x)$Li_2O$)-0.5[0.25$(WO_3)_2$-0.75$P_2O_5$] system when x varies from 0 to 1 are transparent and colorless. Their density (d) and molar volume (V) composition dependencies are shown in Fig. 1.

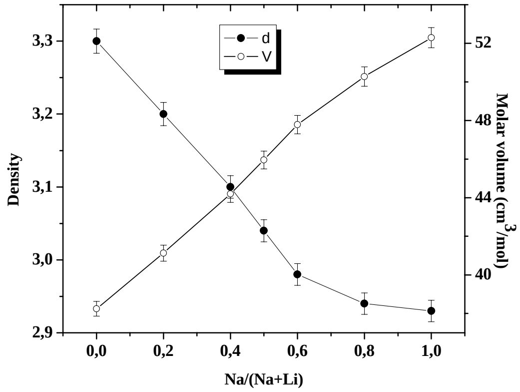

*Fig. 1. Plots of density and molar volume versus the molar ratio Na/(Na+Li) along the system 0.5[x(2NaF)-(1-x)$Li_2O$]-0.5[0.25$(WO_3)_2$-0.75$P_2O_5$].*

It can be noted that the measured density decreases while the molar volume increases as $Li_2O$ is replaced by NaF. The values of density and molar volume are consistent with the ionic size, atomic weight of elements and their amount in these glasses. It can be understood that a more open structure results with incorporation of NaF at the expense of $Li_2O$. Alkali phosphate glasses are composed of tetrahedral units. A decrease in concentration of modifier oxide $Li_2O$ should increase both the concentration of non-bridging bonds P-F and the ratio of terminal and/or intermediate tetrahedral ($PO_xF_y$) units and therefore relatively open structure should result. The temperature dependency of the dc electrical conductivity for $Li_2O$-NaF containing tungsten phosphate glasses is shown in Fig. 2.

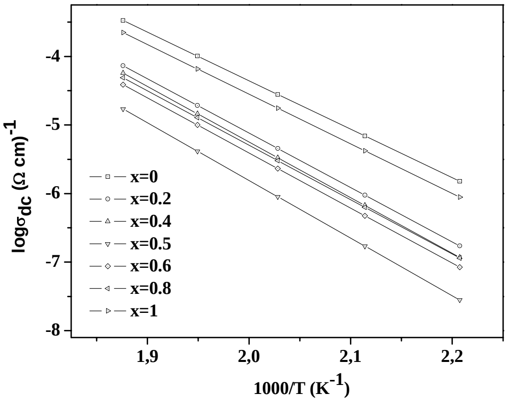

*Fig. 2. Thermal variation of the dc conductivity along the system 0.5 [x(2NaF)-(1-x)$Li_2O$]-0.5 [0.25$(WO_3)_2$-0.75$P_2O_5$].*

It is found that the conductivity follows the Arrhenius law: $\sigma T = \sigma_0 \exp(-Ea/kT)$, where $\sigma$ is the conductivity, $\sigma_0$ is the pre-exponential factor, $E_a$ is the activation energy, k is the Boltzmann constant and T is the absolute temperature. Fig. 3 shows the evolution of the isothermal dc conductivity, in a logarithmic scale (at 473 K and 453 K), as a function of the relative composition ratio Na/(Na+Li). These plots show a flat minimum near x = 0.5. It is worth to notice this minimum is usually observed in mixed alkali glasses [13]. This could be attributed to the maximum of the activation energy (Fig. 3). Compositional glass transition temperature $T_g$ (Fig. 4) and conductivity (Fig. 3) have similar evolution. $T_g$ decreases with increasing the ratio Na/(Na+Li) and reaches a minimum for the value Na/(Na+Li) = 0.5. For Na/(Na+Li) > 0.5, Tg increases. A typical plot of ac conductivity as a function of frequency for (x = 0.6) glass is shown in Fig. 5. The ac conductivity behavior of all the other glasses is qualitatively similar. The ac conductivities exhibit a change of slope to higher values as the frequency is increased. The flattened portion of conductivity curve increases at higher temperatures. The nature of conductivity behavior observed can be explained using Jonsher-type power law [14]. We observed a decrease in the power law exponent from about 0.65 seen in the single-alkali end members to near 0.55 for the mixed alkali compositions. This decrease cannot be attributed to an averaging of the power law exponents found for two single Li- and Na- glasses, since each individually had exponent value larger than 0.55. The lower values of the exponent could indicate lower dimensionality of the conduction pathways in mixed alkali oxide fluoride glasses than that in the single glasses.

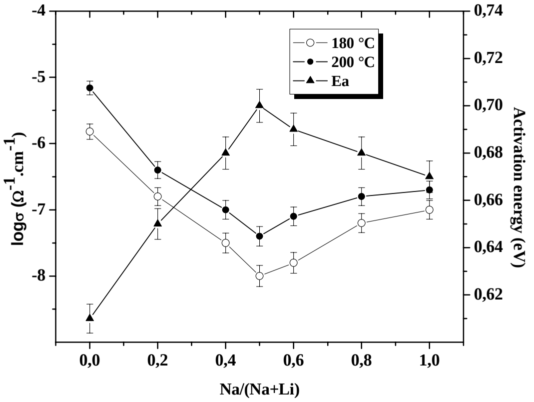

*Fig. 3. Plots of conductivity and activation energy versus composition along the glass system 0.5[x(2NaF)-(1-x) Li$_2$O]-0.5[0.25(WO$_3$)$_2$–0.75P$_2$O$_5$]. Line is drawn as guide to the eye.*

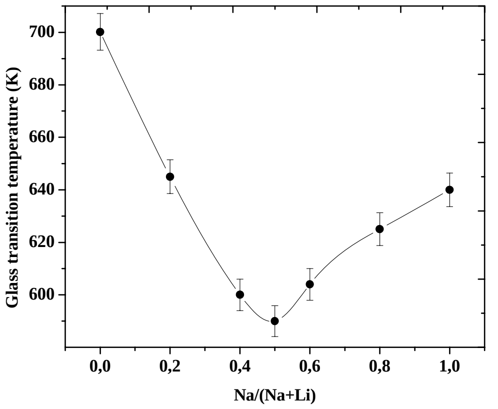

*Fig. 4. Composition change of the glass transition temperature for the glass system 0.5[x(2NaF)-(1-x)Li$_2$O]-0.5[0.25(WO$_3$)$_2$-0.75P$_2$O$_5$]. Line is drawn as guide to the eye.*

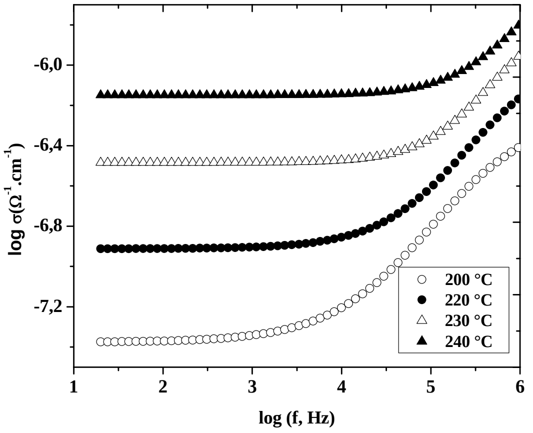

*Fig. 5. Typical example of the ac conductivity of the glass composition 0.5[x(2NaF)-(1-x)Li$_2$O]-0.5[0.25(WO$_3$)$_2$-0.75P$_2$O$_5$] (x = 0.6).*

The complex dielectric modulus formalism ($M^*=1/\varepsilon^*=M'+iM''iwC_0Z^*$) is also used to present the dielectric data of the glasses under study. It allows one to neglect the low frequency long-range conductivity and especially the electrode polarization effect [15]. A plot of the frequency dependence of the normalized imaginary part of M* ($M''/M''_{max}$) for single Li$_2$O, NaF and mixed Li-Na (x = 0.5) glasses at 473K is given in Fig. 6. In each single alkali glass (Li$_2$O or NaF) the modulus peak maximum shifts to higher frequencies as temperature increases. The variation of the frequency corresponding to the maximum of M" versus temperature inverse is of an Arrhenius-type and the activation energy ($E_f$) deduced is close to ($E_\sigma$) issued from dc data; these results suggest that the mechanism of conduction in these single alkali- glasses is probably by 'hopping' process. In addition, the obtained $M''/M''_{max}$ curves are not symmetric, proving a non-exponential behaviour of the conductivity relaxation which can be described by a Kohtrausch function $\Phi(t)=\Phi_0\exp\text{-}(t/\tau_\sigma)^{\beta}$ [16-18]. A more interesting observation obtained in this study is that the relaxation peak appears at a significantly higher frequency, in single Li$_2$O or NaF glasses, than in mixed Li$_2$O-NaF tungsten-phosphate glasses (Fig. 6).

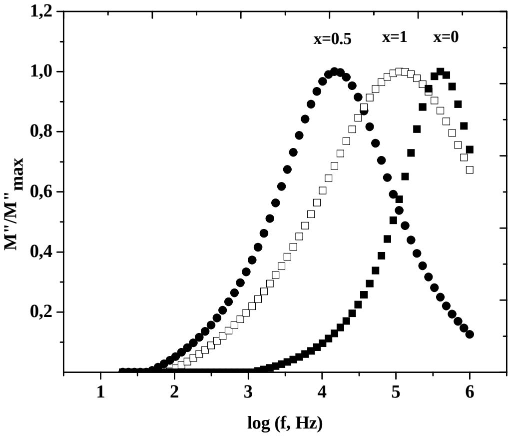

*Fig. 6. Frequency dependence of the imaginary part of the normalized dielectric modulus $M''/M''_{max.}$ for the two single Li and Na and mixed Li-Na (x = 0.5) glasses.*

This behaviour is associated with the mixed alkali effect and indicates the slowing down of the ionic motions both on local and long ranges.

## 4. Discussion

D.Boudlich et al, [19] reported the results of a study of the properties of alkali-tungsten phosphate glasses in the A$_2$O-A$_2$MO$_4$-P$_2$O$_5$ (A= Li, Na; M = W, Mo) systems. The results indicate that A$_2$O, WO$_3$ and P$_2$O$_5$ form stable glasses over a wide and continuous compositional range. The tungsten ions exist in at least two valence states as W$^{5+}$ and W$^{6+}$. The electronic conductivity in these glasses was assumed to be due to electronic hopping from the lower valence state $W^{5+}$ (donor level) to the higher valence state $W^{6+}$ (acceptor level). It is reported also that the presence of high alkali content favours the formation of colorless glasses in which tungsten exists only in the high valency state $W^{6+}$. The glass composition discussed in this paper is based on the general formula $0.5[x(2NaF)-(1-x)Li_2O]-0.5[0.25(WO_3)_2-0.75P_2O_5]$. This basis is used so that glasses have a constant modifier/former ratio and a high modifier content. The latter characteristic will ensure on the one hand that conduction is ionic and on the other hand the absence of the polaron-ion interaction, i.e., the IPE effect. This assumption is confirmed by the absence of any signals in ESR spectra of the $0.5(x(2NaF)-(1-x)Li_2O)-0.5[0.25(WO_3)_2-0.75P_2O_5]$ glass compositions. In other words, there is no or lesser number of $W^{5+}$ ions, so the electronic contribution towards conductivity due to electron charge transfer between different valence states is not seen in the present system.

Moreover, since fluorine in phosphate glasses is mainly present as $-PO_3F$ and $-PO_2F_2$ fluorophosphate terminal groups [20] one can expect that fluorine can not be considered as free carrier charge. On the contrary, if we suppose that fluorine contributes to the conductivity then the $F^-$ anions could be attached to oppositely charged alkali ($A^+$) ions. The natural tendency is for such $A^+$-$F^-$ pairs to move about together as neutral entities. The migration of these pairs does not involve any net displacement of electric charge, so this process will contribute nothing to the electrical conductivity. In this context, when sufficient NaF content is present in the glass, the conductivity will continue to decrease. However, the experimental results (see Fig.3) show that the electrical conductivity increases with NaF content for high Na/(Na+Li) ratios confirming the neutral effect of fluorine on the electrical conductivity of the glasses under study. According to the above arguments, we can conclude that the stabilisation of the tungsten in a high valence state $W^{6+}$ is a predominent condition allowing to neglect the IPE effect and consideration of mixed-alkali effect (MAE) involves the minimum of the conductivity observed for a glass with Na/(Na+Li) = 0.5.

The conductivity related to the mixed-alkali effect (x =0.5) is lower than that of the original $Li_2O$ and NaF single glasses. Indeed, it increases with decreasing temperature (Fig.3). Moreover, the explanation of MAE regularly reported in the literature can be considered either as based upon structural features (e.g., conduction pathways) [21-23] or as based upon differing cation interactions resulting from differences in the mass and/or size of the cation [24,25]. The promising model which takes into account the two features of the MAE is the Dynamic Structure Model (DSM) reported by Bunde et al. and Maass et al. [22,23]. According to this model, the observed minimum of the conductivity in the glasses under study could be attributed to the distinctly different local environment of the two alkali ions, which are preserved in the mixed glasses. Since $Li^+$ and $Na^+$ ions are distinguishable, these sites form clusters (pathways) of various sizes which are intertwined. Note that any vacant site may become occupied by a cation of different nature. When that happened the concerned cation becomes effectively trapped until site relaxation is reconfigured to the newly occupying ion. This trapping mechanism causes a reduction in the overall ionic diffusion [23]. As consequence of such trapping, a decrease in dc conductivity (MAE) is observed (fig. 3). Statistically, it can be noted that a minimum may be pronounced for a composition corresponding to a maximum disorder of alkali elements. Accordingly, the conductivity decreases when we begin substituting lithium by sodium, and a flat plateau or an absolute minimum (Fig. 3) was reached for the composition with the ratio Na/(Na+Li) = 0.5. In addition to ionic conductivity, the glass transition temperature, Tg, which is not directly dependent upon ionic transport, shows a pronounced departure from linearity at intermediate mixed alkali ion compositions. We have also observed that the glass transition temperature is lower for mixed glasses than for the original compositions (x = 0, 1). Such behaviour could also be associated to the 'structural disorder' imposed by the presence of two kinds of cations.

## 5. Conclusions

Analysis of the electrical properties of the $0.5(x(2NaF)-(1-x)Li_2O)-0.5[0.25(WO_3)_2-0.75P_2O_5]$ glasses has been carried out by means of impedance and modulus formalisms. Frequency response of these glasses has been studied over a wide range of temperature and composition using impedance spectroscopy. The conductivity in the studied glass system is found to be dominated by $A^+$ (A = Li, Na) ions showing Arrhenius behavior. The ac conductivity data have been analyzed using Jonsher-type single power law equation. It is found that the power law exponent is lower in mixed alkali glasses suggesting a lower dimension of the diffusion pathways in them. The change of various physical properties, $\sigma_{dc}$ and Tg, versus the ratio Na/(Na+Li) in these glasses is attributed to the mixed-alkali effect (MAE). The observation is qualitatively in agreement with the DSM model, in which the two kinds of cations have distinct local environments.

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