Some physical properties of fluorine oxide glasses belonging to the NaF-Li$_2$O-MoO$_3$-P$_2$O$_5$ system

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The NaF – containing glasses of the 0.5[x(2NaF)-(1-x)Li$_2$O]-0.5[0.4(MoO$_3$)$_2$-0.6P$_2$O$_5$] system, with x varying between 0 and 1, were synthesized. The glass samples have been characterised using powder X-ray diffraction (XRD), thermal analysis, density and impedance spectroscopy. It may be noted that the dc conductivity goes through a minimum for x = 0.5 corresponding to a maximum in the activation energy. This confirms that we have observed the mixed alkali effect (MAE) in the dc conductivity. We have observed lower dimensionality of the conduction pathways in mixed alkali glasses compared to that in the single alkali glasses.

1. Introduction

The advantages of glasses over their crystalline counterparts includes physical isotropy, absence of grain boundaries and a possibility to vary continuously the composition. They are suitable for a wide range of electrochemical applications. Among them phosphate glasses are of particular interest due to the fact that they usually melt at low temperatures, have high thermal expansion coefficients, and good optical transmittance in UV-region. 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} (Ω^{-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]. For example, the introduction of alkali metal fluoride into the phosphate leads to an increase of dc conductivity by about 1 order of magnitude [2,5]. In particular this increase is found in xLiF-(1-x)LiPO$_3$ [2].

It has also found that alkali-oxides, when added to oxide glasses of the system (MoO$_3$-P$_2$O$_5$), act as network modifiers by giving rise to non-bridging oxygens in the structure [6]. Elsewhere, it is reported that conductivity anomalies could exist in transition metal (TM) oxide containing alkali phosphate glasses [7-10]. 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]. Recently, Abbas et al. [11] and Bih et al. [12] by selecting adequate glass compositions in the systems Li$_2$O-Na$_2$O-MoO$_3$-P$_2$O$_5$ and Li$_2$0-Na$_2$O-WO$_3$-P$_2$O$_5$, respectively, have studied the mixed alkali effect (MAE) without interference with IPE effect.

The purpose of this paper is to provide detailed information about the influence of substituting Li$_2$O by NaF on ionic conductivity and some physical properties in the NaF-containing lithium-molybdenum phosphate glasses. By keeping the molybdenum/phosphorus ratio constant and the total concentration of alkali cation very high as 50 mol%, we show that it is possible to investigate the MAE in the 0.5[x(2NaF)-(1-x)Li$_2$O]-0.5[0.4(MoO$_3$)$_2$ - 0.6P$_2$O$_5$] glasses.

2. Experimental

The samples of lithium and sodium molybdenum-phosphate glasses were prepared from appropriate mixtures of reagent-grade Li$_2$CO$_3$, NaF, MoO$_3$ and NH$_4$H$_2$PO$_4$. In order to prevent the excess boiling and consequent spillage, water and ammonia in NH$_4$H$_2$PO$_4$ were removed initially by preheating the mixture at 300 °C for about 12 h. 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.
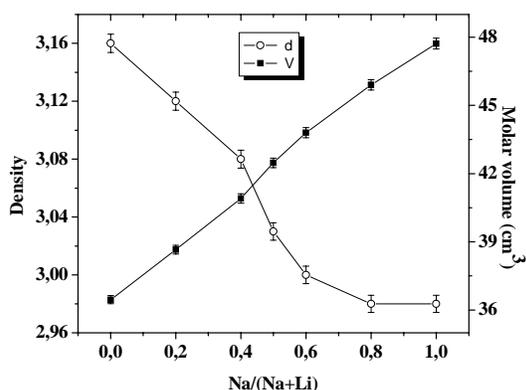
Fig. 1. Plots of density and molar volume versus the molar ratio Na/(Na+Li) along the system 0.5[x(2NaF)-(1-x)Li₂O]-0.5[0.4(MoO₃)₂-0.6P₂O₅].

All prepared glasses have been firstly 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

Transparent glasses of the $0.5(x(2NaF)-(1-x)Li_2O)-0.5[0.4(MoO_3)_2-0.6P_2O_5]$ system were obtained when x varies from 0 to 1. These glasses were subjected to X-ray diffraction studies and no crystalline phases were detected. Their density (d) and molar volume (V) composition dependencies are shown in Fig. 1. It can be noted that the measured density decreases while the molar volume increases as Li₂O is replaced by NaF. The values of density and molar volume are consistent with the ionic size, atomic weight of lithium, sodium and fluorine elements and their amount in these glasses. The temperature dependency of the dc electrical conductivity for Li₂O-NaF containing molybdenum phosphate glasses is shown in Fig. 2. It is found that the conductivity follows the Arrhenius law: $\sigma T = \sigma_0 exp(-Ea/kT)$, where σ is the conductivity, σ_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 displays the isothermal dc conductivity plots, 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 centred 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). Glass transition temperatures T_g were determined by DTA. As can be deduced from Fig.4, T_g decreases with increasing the ratio Na/(Na+Li) and reaches a minimum for the value Na/(Na+Li) = 0.5. Therefore, a similar trend associated with the conductivity MAE is observed for the glass transition temperature. The frequency dependence of conductivity was also investigated for all the compositions as isotherms in a logarithmic scale as shown in Fig. 5 for the composition (x = 0.2). The dynamic conductivity related to the real part of the complex conductivity showed a typical behaviour [14]: a frequency-independent plateau for low frequency range and a power-law increase at high frequencies. 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.
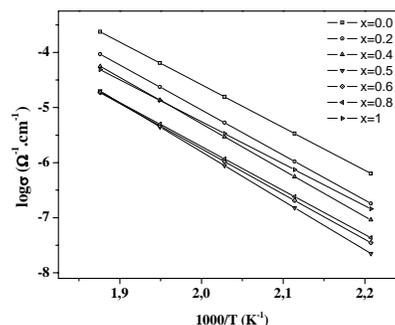
Fig. 2. Thermal variation of the dc conductivity along the system 0.5[x(2NaF)-(1-x)Li₂O]-0.5[0.4(MoO₃)₂-0.6P₂O₅].
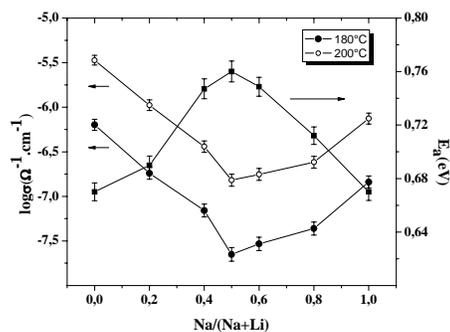
Fig. 3. Plots of conductivity and activation energy versus composition along the glass system 0.5[x(2NaF)-(1-x)Li₂O]-0.5[0.4(MoO₃)₂–0.6P₂O₅]. Line is drawn as guide to the eye.

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 473 K 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_σ) 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 Kohlrausch function $\Phi(t) = \Phi_0 \exp - (t/\tau_\sigma)^\beta$ [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 molybdenum-phosphate glasses (Fig. 6). 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

Apparently the charge carriers which can control the electrical properties of the glasses are: alkali cations, small polaron localised on molybdenum ions and fluorine anion. Such a polaron (or fluorine) could be at the origin of the IPE effect (or cation-anion interaction) which could render the study of MAE effect very difficult. Let us now to argument why the selected $0.5[x(2NaF)-(1-x)Li_2O]-0.5[0.4(MoO_3)_2-0.6P_2O_5]$ glass compositions do not present the IPE effect. Such a result could allow us to study the MAE without any interference with other effects. Since in the $0.5[x(2NaF)-(1-x)Li_2O]-0.5[0.4(MoO_3)_2-0.6P_2O_5]$ glass compositions the Mo/P and O/(Mo+P) ratios are constant, it is obvious to assume that the variation of their electrical properties is not mostly influenced by the structural units of P$_2$O$_5$ and/or MoO$_3$ present in their vitreous networks. However, molybdenum in phosphate glasses might coexist in more than one valence state; thus, electron transfer between Mo cations with two different oxidation forms is permitted. The semi-conducting properties of phosphomolybdate glasses are due to such electron transfer. The presence of Mo^{5+} species in the glass-matrix could results in the interference of MAE and/or IPE effects. The latter effect could be carried out if the glass composition under study ensures that the ion-polaron interactions are neglected. This seems to be realized in highly basic (i. e Li$_2$O-rich) molybdenum-phosphate glasses. The argument is that as the glasses become increasingly oxygen-donor, the formation of the higher oxidation Mo^{6+} is favoured [10]. This result is consistent with the absence of any signals in ESR spectra of the $0.5Li_2O-0.5[0.4(MoO_3)_2-0.6P_2O_5]$ and $0.5(2NaF)-0.5[0.4(MoO_3)_2-0.6P_2O_5]$ glass compositions. Therefore, it could be stated that the electronic conductivity arising by

the inter-valence transfer process between Mo^{5+} and Mo^{6+} is omitted for the glasses corresponding to the total alkali concentration higher than 50 mol%. On the other hand, since fluorine in phosphate glasses is mainly present as -PO$_3$F and -PO$_2$F$_2$ fluorophosphate terminal groups [19] 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. Moreover, one can suggest that fluorine structural role is similar to that of oxygen ion. According to the above arguments, we can conclude that the stabilisation of the molybdenum in a high valence state Mo^{6+} is a predominent condition allowing to neglect the IPE effect and the minimum of the conductivity observed for a glass with Na/(Na+Li) = 0.5 is associated with a MAE effect.
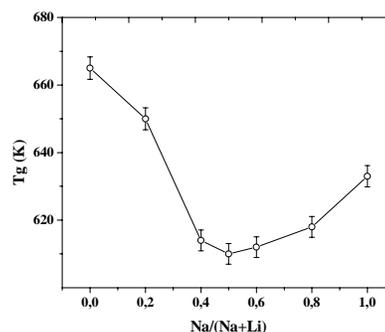
Fig. 4. Composition change of the glass transition temperature for the glass system $0.5[x(2NaF)-(1-x)Li_2O]-0.5[0.4(MoO_3)_2-0.6P_2O_5]$. Line is drawn as guide to the eye.
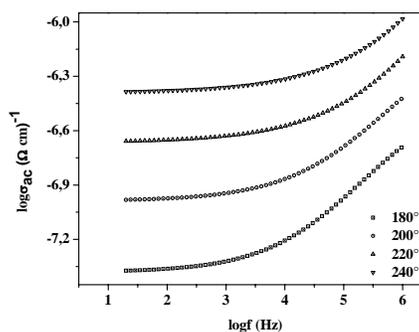
Fig. 5. Typical example of the ac conductivity of the glass composition $0.5[x(2NaF)-(1-x)Li_2O]-0.5[0.4(MoO_3)_2-0.6P_2O_5]$ (x = 0.2).
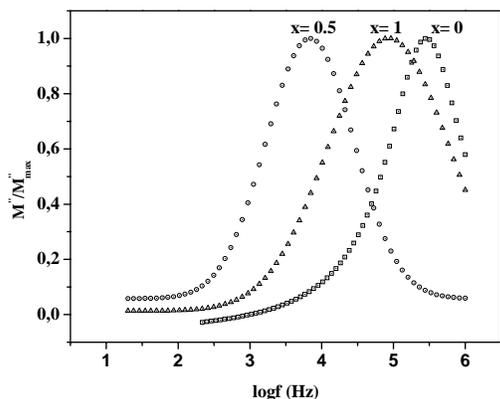
Fig. 6. Frequency dependence of the imaginary part of the normalized dielectric modulus M″/M″$_{max.}$ for the two single Li and Na and mixed Li-Na (x = 0.5) glasses.

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) [20-22] or as based upon differing cation interactions resulting from differences in the mass and/or size of the cation [23,24]. 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. [21,22]. According to this model, the observed minimum of the conductivity in the title phosphate glasses could be attributed to the distinctly different local environment of the two alkali ions, which are preserved in the mixed glasses. The argument is that the atomic characteristics of Li and Na are very different and each cation may reside in a site formed by a local environment in the single glasses as well as in the mixed-alkali compositions. In a single glass where an alkali ion moves into a site previously occupied by the alkali, a sort of structural memory effect [22] favours its migration. However, in the mixed compositions the hopping dynamics of Li and Na cations are intimately coupled with the structural relaxations of the glass network. For instance, to accommodate the jump of a Li^+ cation into a site previously occupied by a sodium cation, the latter must undergo a local relaxation after which the cation can continue to migrate through the matrix. 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 [22]. 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

The change of various physical properties versus the ratio Na/(Na+Li) in mixed Li_2O-NaF molybdenum phosphate glasses, where fluorine anions do not participate in the diffusion process in addition to alkali cations, have provided clearly that mixed alkali in fluorine oxide glasses is similar to that observed in non-fluorine oxide glasses. The occurrence of the minimum in the dc conductivity and a maximum in the activation energy provide clear evidence for the mixed alkali effect in investigated oxide fluoride glasses. Lower dimension of the diffusion pathways has been observed in mixed alkali glasses in comparison to the single alkali glasses. 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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