

Electrical Transport Properties Of Iodine Oxide Phosphate Glasses Issued From The NaI-Li₂O-WO₃-P₂O₅ System

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Abstract: This work concerns the investigation of ion transport behaviour of NaI containing lithium tungsten phosphate glasses in order to understand better the role of NaI in the ionic cation transport. Glasses obtained in the system $0.5[x(2\text{NaI})-(1-x)\text{Li}_2\text{O}]-0.5[0.25(\text{WO}_3)_2-0.75\text{P}_2\text{O}_5]$ 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 effect.

Key words: ion conductivity, glass transition temperature, glasses, tungsten oxide, phosphate and NaI.

I. Introduction

A great deal of attention has been paid to glassy materials for use as solid electrolytes in the fabrication of solid state batteries [1,2]. Besides having high ionic conductivities, glasses have several advantages such as absence of grain boundaries, isotropic properties, ease of thin film formation and greater stability to moisture and iodine diffusion [3]. Many oxide glasses consisting of a glass former (B_2O_3 , P_2O_5 , V_2O_5 , etc.), a metal oxide M_2O ($\text{M} = \text{Ag}$, Li , Na and K) and a doping salt MX ($\text{X} = \text{I}$, Br , Cl and F) were investigated [4-7]. Attempts were made to modify the glass network by mixing a second glass former with the ternary glass system. In these glasses the ionic conductivity was found to be more when compared to ternary glasses with an increase of glass forming region and higher dopant salt concentration.

Molybdate and tungstate glasses are a new family of non-traditional glasses which have been interesting mainly from a scientific point of view. Some of them possess a variety of specific properties due to which they are potential candidates for technological applications as amorphous semiconductors, infrared transmission components, in non linear optical devices, sensors, reflecting windows, soluble microfertilizers, for nuclear waste storage, etc. [8-14]. The main difficulties in the preparation of molybdate or tungstate glasses are connected with the high crystallization tendency of the compositions, because

MoO_3/WO_3 is not able to form a glass itself at a slow cooling rate. All many-component molybdate/tungstate glasses are characterized by two (upper and lower) boundaries of glass formation. From a structural point of view, the first one is related to the possibility to depolymerise the sheet structure of MO_3 containing edge shared MO_6 ($\text{M} = \text{Mo}$, W) octahedra. The other is determined by the compositions containing isolated MO_4 tetrahedra. This peculiarity is important for their practical applications. For example, one of the particular difficulties with the verification of the waste storage is the presence of molybdenum in tetrahedral coordination against the oxygen in the compositions [14]. That is why it is interesting to control the structure of molybdenum or tungsten in the glasses.

Recently [15-18], 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) [15]. More recently, Abbas et al. [19] and Bih et al. [20] by selecting adequate glass compositions in the systems $\text{Li}_2\text{O}-\text{Na}_2\text{O}-\text{MoO}_3-\text{P}_2\text{O}_5$ and $\text{Li}_2\text{O}-\text{Na}_2\text{O}-\text{WO}_3-$

P₂O₅, 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(2NaI)-(1-x)Li₂O]-0.5[0.25(WO₃)₂-0.75P₂O₅] glasses at high alkali compositions, with the view for stabilization of tungsten in the high valency state W⁶⁺, 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%.

II. Experimental

The samples of lithium and sodium tungsten-phosphate glasses were prepared from appropriate mixtures of reagent-grade Li₂CO₃, NaI, WO₃ and NH₄H₂PO₄. In order to prevent the excess boiling and consequent spillage, water and ammonia in NH₄H₂PO₄ 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 characterized 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 orthophthalate 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.

III. 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(2NaI)-(1-x)Li₂O)-0.5[0.25(WO₃)₂-0.75P₂O₅] system when x varies from 0 to 1 are transparent and colorless. The temperature dependency of the dc electrical conductivity for Li₂O-NaI containing tungsten phosphate glasses is shown in Fig.1. It is found that the conductivity follows the

Arrhenius law: $\sigma T = \sigma_0 \exp(-E_a/kT)$, 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.2 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 $x = 0.6$. It is worth to notice this minimum is usually observed in mixed alkali glasses [21]. This could be attributed to the maximum of the activation energy (Fig. 3).

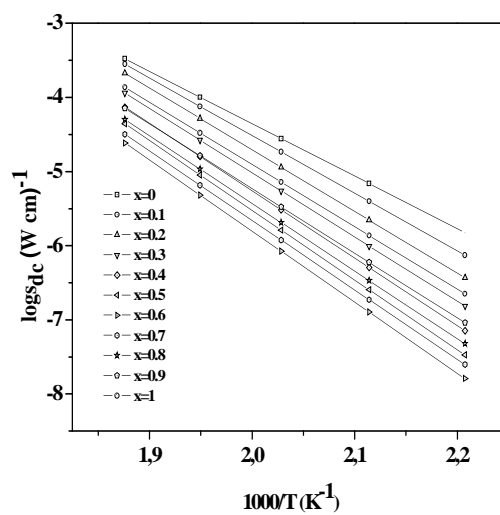


Fig. 1: Thermal variation of the dc conductivity along the system 0.5[x(2NaI)-(1-x)Li₂O]-0.5[0.25(WO₃)₂-0.75P₂O₅].

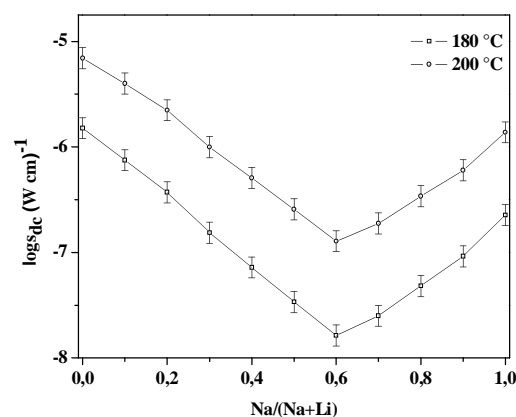


Fig. 2: Plots of conductivity versus composition along the glass system 0.5[x(2NaI)-(1-x)Li₂O]-0.5[0.25(WO₃)₂-0.75P₂O₅]. Line is drawn as guide to the eye.

Compositional glass transition temperature T_g (Fig.4) and conductivity (Fig.2) 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, T_g increases.

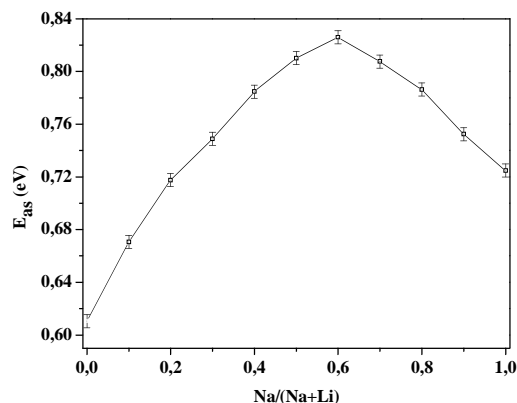


Fig. 3: Activation energy versus composition along the glass system $0.5[x(2\text{NaI})-(1-x)\text{Li}_2\text{O}]-0.5[0.25(\text{WO}_3)_2-0.75\text{P}_2\text{O}_5]$. Line is drawn as guide to the eye.

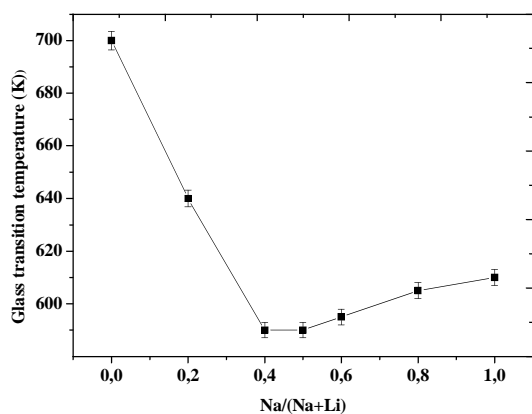


Fig. 4: Composition change of the glass transition temperature for the glass system $0.5[x(2\text{NaI})-(1-x)\text{Li}_2\text{O}]-0.5[0.25(\text{WO}_3)_2-0.75\text{P}_2\text{O}_5]$. Line is drawn as guide to the eye.

A typical plot of ac conductivity as a function of frequency for ($x = 0.2$) glass is shown in Fig. 5. The ac conductivity behaviour 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 behaviour observed can be explained using Jonsher-type power law [22]. 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.

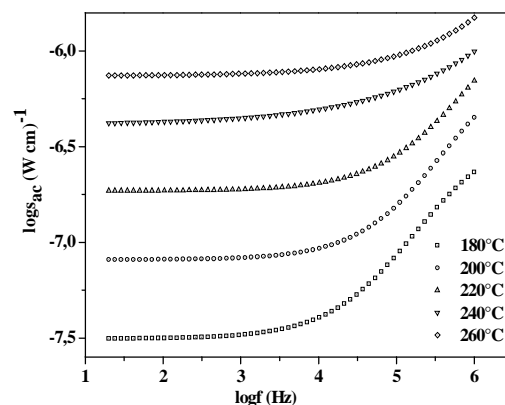


Fig. 5: Typical example of the ac conductivity of the glass composition $0.5[x(2\text{NaI})-(1-x)\text{Li}_2\text{O}]-0.5[0.25(\text{WO}_3)_2-0.75\text{P}_2\text{O}_5]$ ($x = 0.2$).

The complex dielectric modulus formalism ($M^* = 1/\epsilon^* = M' + iM'' = i\omega C_0 Z^*$) 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 [23]. A plot of the frequency dependence of the normalized imaginary part of M^* (M''/M''_{max}) for single Li_2O , NaI and mixed Li-Na ($x = 0.6$) glasses at 473K is given in Fig. 6. In each single alkali glass (Li_2O or NaI) the modulus peak maximum shifts to higher frequencies as temperature increases.

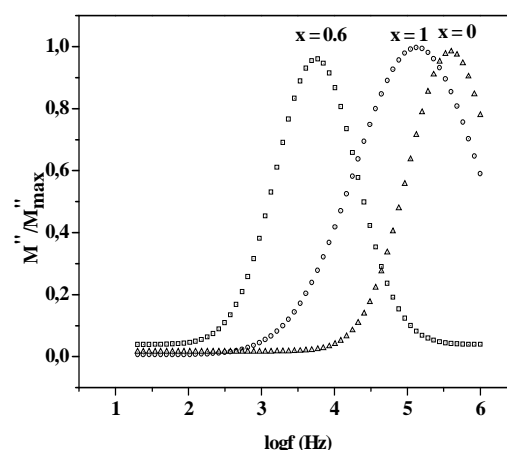


Fig. 6 : Frequency dependence of the imaginary part of the normalized dielectric modulus M''/M''_{max} for the two single Li and Na and mixed Li-Na ($x = 0.6$) glasses.

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 behavior of the conductivity relaxation which can be described by a Kohtrausch function $\Phi(t)=\Phi_0\exp(-(t/\tau_\sigma)^\beta)$ [24-26]. A more interesting observation obtained in this study is that the relaxation peak appears at a significantly higher frequency, in single Li₂O or NaI glasses, than in mixed Li₂O-NaI tungsten-phosphate glasses (Fig. 6). This behavior is associated with the mixed alkali effect and indicates the slowing down of the ionic motions both on local and long ranges.

IV. Discussion

The properties of alkali-tungsten phosphate glasses in the A₂O-A₂MO₄-P₂O₅ (A= Li, Na; M = W, Mo) systems have been reported earlier by us [27]. The results indicate that A₂O, WO₃ and P₂O₅ form stable glasses over a wide and continuous compositional range. The tungsten ions exist in at least two valence states as W⁵⁺ and W⁶⁺. It is reported also that the presence of high alkali content favours the formation of colourless glasses in which tungsten exists only in the high valency state W⁶⁺. This basis is used so that the glasses under study - in the present work - have a constant modifier/former ratio and high modifier content. The glass composition discussed in this paper is based on the general formula 0.5[x(2NaI)-(1-x)Li₂O]-0.5[0.25(WO₃)₂-0.75P₂O₅]. 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(2NaI)-(1-x)Li₂O)-0.5[0.25(WO₃)₂-0.75P₂O₅] glass compositions. In other words, there is no or lesser number of W⁵⁺ ions, so the electronic contribution towards conductivity due to electron charge transfer between different valence states is not seen in the present glasses. Therefore, one can state that the stabilization of the tungsten in a high valence state W⁶⁺ is a predominant 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) = 0.6.

The conductivity related to the mixed-alkali effect (x = 0.6) is lower than that of the original Li₂O and NaI single glasses. Indeed, it increases with decreasing

temperature (Fig.2). Moreover, the explanation of MAE regularly reported in the literature can be considered either as based upon structural features (e.g., conduction pathways) [28-30] or as based upon differing cation interactions resulting from differences in the mass and/or size of the cation [31,32]. 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. [29,30]. 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 [30]. As consequence of such trapping, a decrease in dc conductivity (MAE) is observed (fig. 2). 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. 2) was reached for the composition with the ratio Na/(Na+Li) = 0.6. In addition to ionic conductivity, the glass transition temperature, T_g, 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 behavior could also be associated to the 'structural disorder' imposed by the presence of two kinds of cations.

V. Conclusion

Analysis of the electrical properties of the 0.5(x(2NaI)-(1-x)Li₂O)-0.5[0.25(WO₃)₂-0.75P₂O₅] 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 behaviour. 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, σ_{dc} and T_g , 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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