IONIC AND ELECTRONIC CONDUCTIVITY OF SODIUM IODIDE AND LITHIUM TUNGSTEN PHOSPHORUS OXIDE GLASSES

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Abstract. Morocco exports phosphates and is exploring new applications for local phosphate mining resources, we have turned our attention to phosphate materials derived from the xNaI-(0.5-x)Li_2O-0.125WO_3-0.375P_2O_5 with (x=0, 0.1, 0.2, 0.25, 0.3, 0.4, 0,5). Phosphate glasses are less durable than silicate glasses; lithium replaces sodium, causing structural changes. This study focuses on the electrical conductivity of oxide glasses in the xNaI-(0.5-x)Li_2O-0.125WO_3-0.375P_2O_5, and in particular the effect of incorporating two modifiers - or the effect of mixed alkalis. The results are noted as:(i)the mixed-alkali glasses (Li/Na) exhibit slower dissolution and higher chemical durability than single-alkali glasses, with the strongest durability enhancement around Na/(Na+Li) ≈ 0.5–0.6; (ii)The mixed-alkali effect (MAE) reduces alkali ion mobility, which suppresses proton exchange and slows dissolution; larger alkali ions contribute most to the MAE; (iii) Dissolution and conductivity are non-additive: glasses with only Li or Na are more conductive (Li > Na) and have lower activation energies, while MAE introduces a pronounced minimum in conductivity at certain compositions (near Na/(Na+Li) ≈ 0.6) and can raise the activation energy there; (iiii) In phosphate glasses, introducing alkalis lowers melting temperature but increases water sensitivity; MAE arises from redistribution/mobility changes of Li and Na ions within the phosphate network.

1 Introduction

Ion conduction properties in glassy materials are predicted on the basis of chemical bonding considerations and specific structural and thermal criteria. They are determined as a function of temperature over a wide range of frequencies. Electrical performance can be optimized by modifying the chemical composition of materials through appropriate substitutions. In glass science, the mixed alkali effect (MAE) is a more intriguing phenomenon, which is observed in ionically conductive glassy and crystalline systems, where the total mixed cation content is kept constant, while the relative cation content is changed. Because ionic transport plays such an important role in modern high-tech applications of glassy electrolytes. Electrolyte applications include electrochemical energy storage (primary or secondary lithium-anode generators), sensors (pH or alkali cation-specific electrodes) and optoelectronics (ion-exchange waveguides). The study of MAE related to ionic transport is very important for the purpose of application and understanding the diffusion mechanism of alkali ions. The most pronounced mixed alkaline effect occurs at the ionic conductivity σ_{dc}, which represents long-range ionic transport. In a mixed-alkali glass system, the σ_{dc} conductivity passes through a pronounced minimum, when the proportions, of two or more alkali or alkaline earth modifier oxides, are approximately equal in concentration [1]. The magnitude of MAE has long been a subject of research into mixed-modifier oxide glasses. Dynamic properties such as: chemical durability, viscosity, coefficient of friction, coefficient of thermal expansion, diffusion coefficient, glass transition temperature of mixed alkali glasses exhibit a marked non-linear behavior. In the literature, various models have been proposed to explain the magnitude of MAE and have been applied in several previous studies. These models assume either a broad structural change induced by mixing of modifier cations of different sizes, or a specific interaction between these cations. Neither of these hypotheses has been observed experimentally [2]. A few years later, Greaves et al [3], obtained data using the EXAFS method indicating that the environment of mobile cations in the glassy lattice is well determined by the type of cation that "creates″ the site it occupies. Bunde and al, [4] based on the latter result and proposed a new model for ionic transport in glass, called "Dynamic Structure″ Model (DSM)". The main idea of the DSM model is the existence of disparities between the different types of sites designated by cations in the glass network. Ion migration is associated with a

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'memory effect' of previously occupied sites, leading to the creation of the ionic pathway. In addition, structural results [5] and molecular dynamics simulations [6] confirm that the environment for different types of cations differs from one cation to another. The low mobility of cations in mixed alkali glasses is linked to the relaxation time required to arrange cation sites of different types. The random distribution model (RDM) [2] is based on almost the same arguments as DSM.

The Mixed Alkali Effect (MAE) is assumed to be a consequence of random mixing of ions of different types and with different environments, leading to a 'short-range migration path' for each alkali type. However, this model did not introduce any possible site reorganization. In this work, we investigate the possibility of site relaxation associated with MAE. Site relaxation implies a reorganization of the local lattice to arrange the sites of cations of different types, in order to test this possible local cooperation between mobile cations and lattice. We analysed the effect of mixed alkali (MAE) in the glassy system xNaI-(0.5-x)Li_2O-0.125WO_3-0.375P_2O_5.

The aim is then to clarify why the conductivity σ_{dc}, the relaxation time τ_σ passes through a pronounced minimum when the modifier oxides present are in approximately equal proportions. The explanation of ionic conduction mechanisms requires knowledge of the structure of these oxides. The results obtained by impedance spectroscopy can be directly compared with those obtained by the IR spectroscopic method which will be presented in the course of this work.

2 Experimental procedures

The synthesis process of the glasses has been described elsewhere [8]. The vitreous state of the samples was analysed through X-ray diffraction (XRD) and differential scanning calorimetry (DSC) studies. The density measurement was taken by the Archimedes method.

For measurements of electrical conductivity, silver electrodes of 5mm diameter were applied onto two opposite sides of the samples. The average thickness of the glasses was 0.5 to 1mm. The electrical properties of samples were studied by an impedance /admittance spectroscopy method. The spectra were carried out on a Hewlett Packard Model 4284A precision LCR Meter in the frequency range 20 to 106 Hz and at temperatures from 20 to 260°C.

The chemical durability of the glasses was estimated in term of the dissolution rate (D_R). This later was calculated from the measured weight loss (ΔW) using the equation (1) [9]:

$$D_R = \frac{\Delta W(g)}{A(cm^2)\times t(min)} \quad \text{(eq. (1))}$$

where A is the surface area (cm^2) of the sample and t is the time (min) that the sample was immersed in the test solution at 32 °C. The tests were performed in medium having different pH values. The buffer solution from 5.5 to 8.5 pH were prepared by taking 2.5 vol % glacial acetic acid in water and by adding concentrated ammonia solution until the desired pH value was reached. The pH of the solution was measured using a digital pH-meter (micro pH 2000 Crison). Leaching was performed by placing 0.2 g of glass and 100 ml of the ammonia acetate buffer solution into Erlenmeyer flasks, with pH's from 5.5 to 8.5, for specific time intervals, at a constant temperature 32°C.

3 Results and discussion

Figure 1 shows an increase in density as a function of x=Na/(Na+Li). The linear density behaviour shows that each oxide in the glass contributes to the density with a specific factor [10]. The increase in density with the substitution of Li_2O by NaI is in agreement with the decrease in the fraction of ionic character (FCI (Li-O)=0.78; FCI (Na-I)=0,53). These values are closely linked to glass composition. In fact, the increase in density can still be explained by the decrease in bond strength Li-O ((dissociation energy E_d(Li-O)=341 kj/mol) in relation to Na-I (dissociation energy E_d(Na-I)=301 kj/mol of glass following substitution of Li_2O for NaI.

Similar behaviour is observed for molar volume. In the glasses studied here, the contents of P_2O_5 and WO_3 are fixed, while Li_2O is substituted by NaI. Thus, the oxygen/(tungsten + phosphorus) ratio is changed by substituting Li_2O with NaI. As a result, there will be a significant change in the relative number of PO_4 et WO_n (n=4,6). Considering the volumes of the ions Li^+ (Vi=8 cm^3) and Na^+ (Vi=11.2 cm^3) [11]. It can be concluded that the linear increase in V_m is due to a growth in the free volume of the glass following the substitution of base Li_2O to NaI. The linear molar volume behaviour indicates that the glass matrix P_2O_5-WO_3 depends on the addition of alkalis. This increase in molar volume may be due to an increase in the volume of the polyhedral formed.

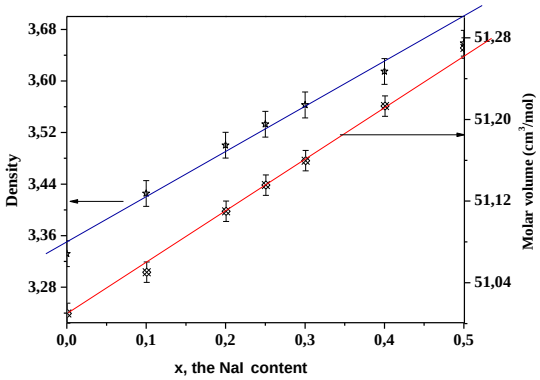

Fig. 1. The density and the molar volume at 25 °C as a function of the Na/(Na+Li) molar ratio of the xNaI-(0.5-x)Li_2O-0.125WO_3-0.375P_2O_5 glasses. Line is drawn as guide to the eye.

In this section, we will study chemical durability in mixed alkali glasses xNaI-(0.5-x)Li_2O-0.125WO_3-0.375P_2O_5. Figure 2 illustrates the evolution of the dissolution rate D_R for glasses in the xNaI-(0.5-x)Li_2O-0.125WO_3-0.375P_2O_5 based on the ratio Na/(Na+Li). Measurement temperature is constant (32°C). Results are given for pH solutions ranging from 5.5 to 8.5.

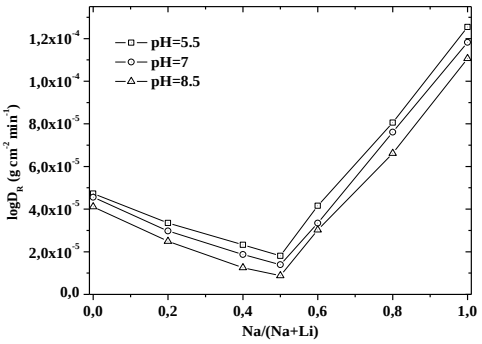

Fig. 2. Change in dissolution rate (D_R) as a function of ratio Na/(Na+Li).

Dissolution rate tests show that glasses in the xNaI-(0.5-x)Li_2O-0.125WO_3-0.375P_2O_5 are susceptible to degradation in acidic, neutral or basic environments. The most chemically durable composition is that corresponding to the ratio Na/(Na+Li) = 0.5. The minimum DR can be seen as the result of the minimum ionic mobility when the proportions of Na and Li are equal. The reaction between water and silicate glasses results in the replacement of bridging oxygens by non-bridging oxygens in the structure [12]. This replacement of bridging oxygens reduces the connectivity of the glass network and leads to a decrease in chemical durability and glass transition temperature [12] and increases the recrystallization tendency of glass [13]. Several jobs [14] have reported that the rate of dissolution at a given temperature increases with increasing alkali oxide content in alkali silicate glasses.

Single-alkali glasses NaI or Li_2O have higher dissolution rates than mixed-alkali glasses, so single-alkali glasses NaI have higher dissolution rates than Li_2O. This is due to the weaker bond strength of sodium-iodine than lithium-oxygen. Cations (Na and/or Li) will have a greater disrupting effect on the structure, forming linear chains at the expense of three-dimensional ones, and will tend to interrupt the glassy network.

There may be another factor to consider in terms of the interest of these results. This particular system is a mixed alkali system, and this system shows the presence of the mobile ion effect. A big change in dynamic properties can occur when a fraction of one mobile ion is replaced by another type of mobile ion.

It is also well known that reducing the mobility of alkali ions in glass increases its chemical durability [15-17]. Thus, some chemical and physical properties vary in an extremely non-additive way if one alkaline oxide is gradually replaced by another in a glass. Chemical durability increases markedly when one alkaline oxide is replaced by another [15,18]. In an acidic, neutral or basic medium, the chemical attack mechanism involves the exchange of alkali ions from an alkali-ion-containing glass by protons from the surrounding medium, so the chemical durability of mixed alkali glasses has the same mechanism as that of single alkali glasses. In glasses where alkali ion mobility controls the rate of proton exchange, the lower alkali ion mobility in mixed alkali glasses should decrease the rate of glass dissolution.

Introducing alkalis into phosphate glass has the advantage of significantly lowering the glass's melting temperature. On the other hand, the glass becomes much more sensitive to water. Q^2 and Q^1 units appear in the phosphate network, weakening the structure glass (depolymerization of the phosphate network). In addition, the nature of the alkali influences glass weathering. For example, Bunker shows that at 60°C, a glass 0.3Li_2O-0.7SiO_2 [19] dissolves twenty times more slowly than 0.3Na_2O-0.7SiO_2 [20], which itself dissolves six times more slowly than 0.3K_2O-0.7SiO_2 [21]. We already know that the departure of larger cations creates high-volume cavities that facilitate water penetration.

The influence of the mixed alkali effect on the chemical durability of the glass was determined by gradually replacing Li_2O with NaI in the glasses xNaI-(0.5-x)Li_2O-0.125WO_3-0.375P_2O_5. As shown in Fig. 2, the amount of dissolved glass is lowest at Na/(Na+Li)=0.5; where the minimum mixed alkali effect occurs. The chemical durability of mixed alkali glass is almost five times greater than that of a single alkali glass.

Fig. 2 shows the dissolution rate as a function of the ratio Na/(Na+Li), it is clearly shown that the dissolution rate passes through a minimum at a particular composition. Qualitatively, the quantity of alkali ions leached varies with the mobility of the more mobile alkali ions. As a result, the higher durability of mixed alkali glasses is essentially due to the lower mobility of alkali ions, which reduces the rate of proton penetration into these glasses. Under conditions where the mechanism of chemical corrosion is controlled by the exchange of alkali ions by protons, rather than congruent dissolution of the glass, the highest chemical durability would be expected at a composition where the mobility of the most mobile alkali ion is lower, near the point of intersection.

It has been shown that the addition of a third oxide such as: Al_2O_3 [16], CaO [16] and TiO_2 [17] etc. in alkaline silicate glasses do not have a considerable effect on the reduction in alkali ion mobility that results from the effect of mixed alkalis. It may also be considered that the addition of a mixed alkali to phosphate glasses simply leads to a change in the location or distribution of these two alkali ions in the glass framework, or to a redistribution of these ions without any influence on the combination form and structure of the glass.

The influence of the mixed alkali effect on chemical durability is mainly due to the reduction in alkali ion mobility as the mobility of larger alkali ions is greatly reduced; this can be demonstrated by measuring the change in Li^+ and Na^+ content in the solution. Analysis of the composition of the etching solution and the glass surface has shown that the mixed alkali effect results mainly from a reduction in the mobility of the larger ion. The "maximum value" appears in the case of larger ions. Diffusion and exchange of alkali ions are thought to control the dissolution process. Thus, optical glasses with improved chemical durability can be obtained by means of the mixed alkaline effect. A study by Dilmore and colleagues [22] has shown that MAE occurs only when certain specific conditions are met. The

substitution of Li_2O by NaI decreases the diffusion movement of the Na ion and consequently the ionic exchange between the protons of the etching solution and the alkaline ions of the glass decreases, resulting in a decrease in Na mobility, which means that the minimum dissolution rate when the proportions of Li and Na cations are approximately equal, which refers to the decrease in ionic exchange rates between etching solution -glass surface.

Conductivity measurements were carried out on this series between 25°C and 260°C, i.e. in a temperature range below that of the glass transition and crystallization determined by ATD. The results obtained using the complex impedance method are plotted on a diagram. $Log(\sigma_{dc}) = f(10^3/T)$ shown in figure 3. A set of roughly parallel straight lines can be seen, indicating that the conductivities of these glasses follow an Arrhenius law and that their activation energies are close to each other.

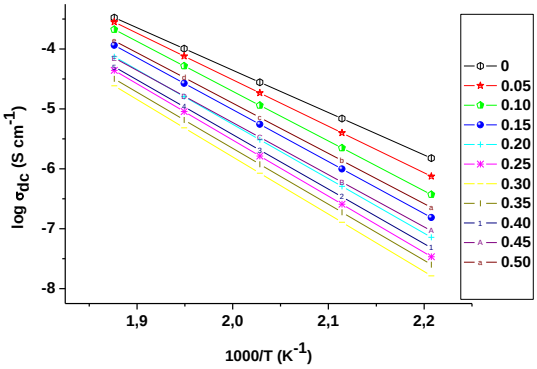

Fig. 3. Change of the logarithm of electric conductivity for the investigated xNaI-(0.5-x)Li_2O-0.125WO_3-0.375P_2O_5 glasses versus 1/T.

In order to demonstrate the mixed alkaline effect, we have plotted $Log_{10}(\sigma_{dc}) = f(x)$, at different temperatures, with x =Na/(Na+Li) is the cationic mole fraction in each glass system. Figure 4 shows the conductivity σ_{dc} of the glass system xNaI-(0.5-x)Li_2O-0.125WO_3-0.375P_2O_5. Conductivity passes through a pronounced minimum when the Na/(Na+Li) ionic ratio is equal to 0.6, this phenomenon is known as the mixed alkaline effect, and the magnitude of this effect becomes greater at lower temperatures.

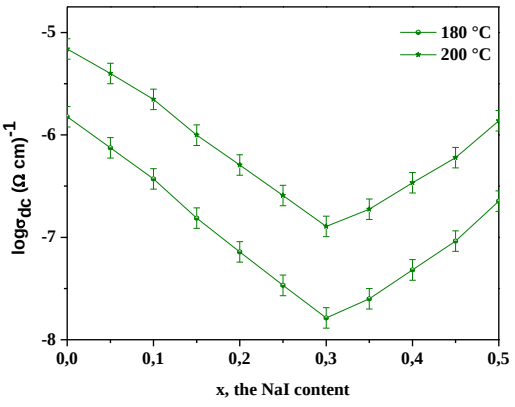

Fig. 4. Variation of the logarithm of the dc conductivity for the glasses xNaI-(0.5-x)Li_2O-0.125WO_3-0.375P_2O_5 as a function of the relative Na alkali ratio. Line is drawn as guide to the eye.

Activation energies can also be determined from Figure 3. Figure 5 shows the activation energy as a function of the Na/(Na+Li) ratio of the glassy system xNaI-(0.5-x)Li_2O-0.125WO_3-0.375P_2O_5. We observe that this magnitude (Ea) passes through a maximum when the Na/(Na+Li) ionic ratio is equal to 0.6.

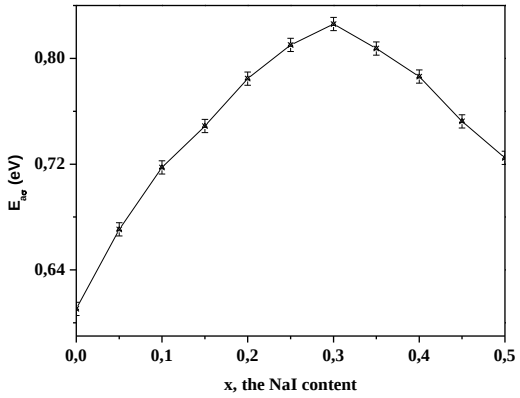

Fig. 5. Activation energy E_a obtained from dc conductivity for the glasses xNaI-(0.5-x)Li_2O-0.125WO_3-0.375P_2O_5 as a function of Na alkali relative ratio. Line is drawn as guide to the eye.

Glass with a Na/(Na+Li) ionic ratio of 0.6 show overall low ionic mobility. A comparison of single and mixed cation glasses is shown in figure 3. Mixed alkali (MA) and single alkali (SA) glasses share the same characteristics: an increase in ionic conductivity σ_{dc} and a decrease in activation energy in proportion to the mobile cation in the glass system. So the more conductive a glass, the lower its activation energy. For single-cation glasses (SA), lithium glasses are more conductive than sodium glasses of similar composition. This is due to the greater ionic mobility of lithium glasses compared to sodium glasses. Furthermore, as shown in Figure 3, conductivity does not vary linearly with the mole fraction of alkali. This indicates that not all lithium and sodium cations are mobile, i.e. a number of lithium and sodium cations participate in the formation of the glass lattice, while those acting as lattice modifiers retain their mobility. The fixation of lithium and sodium in the lattice can be correlated with the existence of oxygens not bound to phosphorus in glasses very rich in lithium and sodium. This would imply that lithium and sodium ions bound to phosphate groups are the most mobile. Mixed alkali glass (0.3NaI-0.2Li_2O-0.125WO_3-0.375P_2O_5 shows the lowest conductivity. It is due to the decreased mobility of the modifier cations (Li and Na), which reflects the reduction in local cation conduction space coordination (CLCS). We believe that this reduction in CLCS can be interpreted in the framework of the unified site relaxation model as a consequence of the creation of unsuitable or energetically unfavourable sites in the local vicinity of a given cation. The results we obtained for mixed alkali glasses are qualitatively in good agreement with the results of Ingram and colleagues [3]

who studied glasses $Ag_5I_4BO_2$. It has been suggested that the mixed alkali effect may be due to changes in the mobility of alkali ions in the glass. An increase in the concentration of one type of alkali ion increases its mobility, in turn the mobility of the other type of ion decreases due to the decrease in its concentration. The general behavior of T_g in composition can be explained by considering that the mobility of Li^+ ions is greater than that of Na^+ ions, due to the greater molar volume of Na^+ ions compared to Li^+ ions.

As shown in Fig. 6, conductivity is frequency-dependent; at a given composition, conductivity increases with increasing frequency, the mixed alkaline effect is found to be more pronounced at low frequencies, and the magnitude of MAE is reduced if the frequency is progressively increased (Fig. 6). The magnitude of MAE decreases as the C_{tot} concentration of mobile ions decreases [23], MAE decreases with the addition of an oxide former Al_2O_3 and tends to disappear with the addition of 8% Al_2O_3 to the mixed alkaline (Li, Na) phosphate glass system [24]. The magnitude of MAE decreases if the two different mixed alkaline types have similar ionic radii.

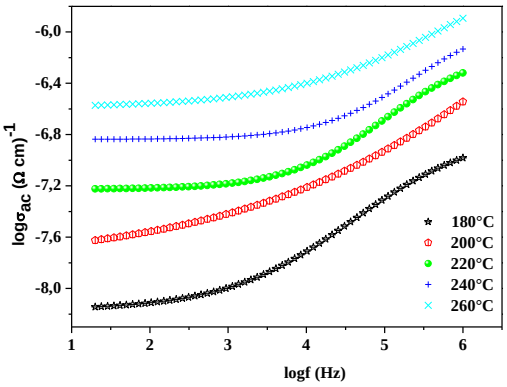

Fig. 6. The ac conductivity of the glass 0.4NaI-0.1Li_2O-0.125WO_3-0.375P_2O_5

Figure 7 shows the dielectric constant ε' (ε'=1/M') as a function of log(f) for glasses xNaI-(0.5-x)Li_2O-0.125WO_3-0.375P_2O_5 at different temperatures. At lower frequencies or conductivity plateaus σ_{dc}, the dielectric constant (ε'=1/M') glass (MA) are higher than that of glass SA. In other words, at higher frequencies, the dielectric constants of glasses MA are smaller than those of glass SA. These results are consistent with those found by Prasad [25]. The dielectric constant of mixed-alkali calcium silicate glass at 40 GHz and constant temperature is lower than that of corresponding single-alkali glasses [25]. Also, the dielectric constant of Na_2O-K_2O-SiO_2 glasses measured at 3.1 MHz and at room temperature is smaller than that of corresponding SA glasses [26].

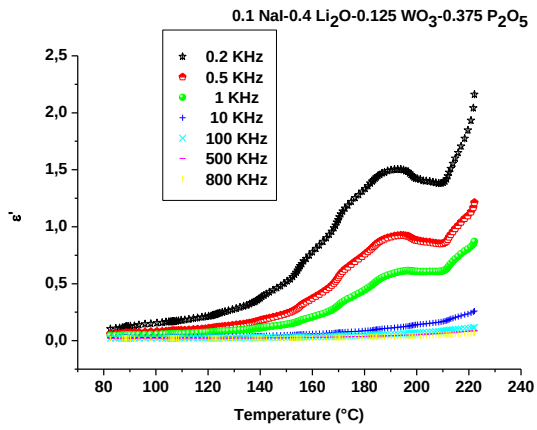

Fig. 7. Variation of the ε' for the glass 0.1NaI-0.4Li_2O-0.125WO_3-0.375P_2O_5 as a temperature.

We have also plotted the normalized imaginary part M''/M''_{max} in figure (8) of mixed alkali glasses and single alkali glasses at different temperatures. At a given temperature, these spectra show asymmetrical peaks centred approximately in the dispersion region of M^*. A characteristic frequency f_p corresponds to this M'' maximum. The frequency range to the left of the peak corresponds to long-range movements of mobile ions, and the range to the right of the peak corresponds to ions more confined in their potential wells. The small frequency range in which the peak is observed corresponds to the transition from short-range to long-range mobility at decreasing frequency [27]. Quantitatively, it is defined by the relation $\omega\tau_\sigma=1$ where τ_σ represents the most probable conductivity relaxation time [28]. As temperature increases, the maxima of the asymmetrical M'' peaks shift towards higher frequencies. [29]. On either side of the peak frequency, the asymmetrical curves of M"/M "$_{max}$ as a function of frequency are consistent with a non-exponential behaviour of conductivity relaxation. The width of the peak at half-height is much greater than that of the Debye behavior [29]. As a result, for the Kohlrausch parameter, the β value of mixed-alkali glasses is lower than that of single-alkali glasses.

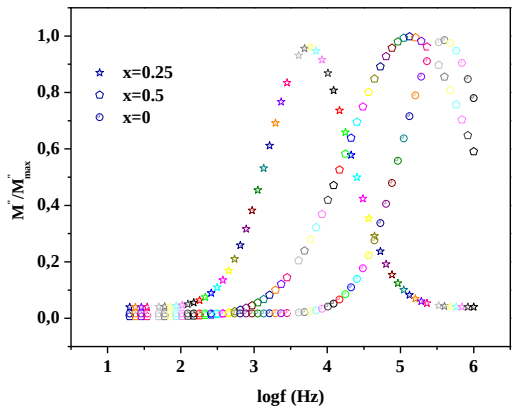

Fig. 8. Frequency dependence of the imaginary part of the normalized dielectric modulus M"/M"max. for the two single Li and Na and mixed Li-Na glasses.

IR spectrum interpretations are mainly based on spectral libraries, which are particularly well-stocked and up-to-date in the field of organics. However, when it comes to elucidating the structure of a mineral species, we have few reference spectra at our disposal. As a result, other techniques (NMR, Raman, EPR, XPS, etc.) provide more information. However, studies carried out [1,5,6,30] analyzed vitreous phosphate materials using infrared spectroscopy. We therefore decided to update and complete the studies already carried out on glass analysis xNaI-(0.5-x)Li_2O-0.125WO_3-0.375P_2O_5. After creating a library of the most exhaustive spectra in the field, we examined the IR spectra of these glasses.

Our aim is not to reconstruct the precise structure of the glasses we produce, but to interpret the most frequently observed infrared absorption bands. IR spectra of glasses xNaI-(0.5-x)Li_2O-0.125WO_3-0.375P_2O_5 in the 400-4000 cm^{-1} range are shown in figure 9.

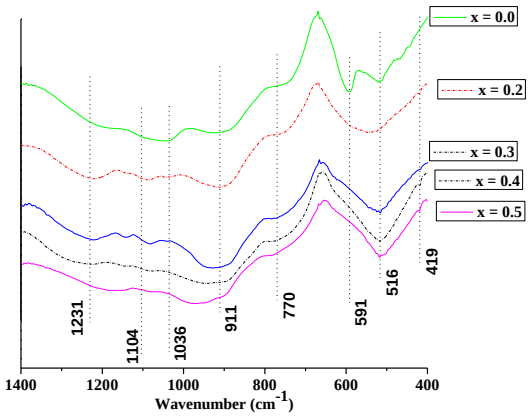

Fig. 9. Infrared spectra of oxide glasses in the system xNaI-(0.5-x)Li_2O-0.125WO_3-0.375P_2O_5.

Spectra of the glasses of the series xNaI-(0.5-x)Li_2O-0.125WO_3-0.375P_2O_5 have the following general characteristics:

1st domain: of 400 à 800 cm^{-1}.

- The presence of a very wide and intense band at 521 cm^{-1}, this band attributed to the deformation of phosphate groups with a possible contribution of LiO_4 and WO_4. It is observed that the frequency of this band passes through a minimum when the two alkali oxides are approximately in equal proportions.

- A band centered at 632 cm^{-1} of low intensity is attributed to the symmetric W-O-W stretching frequency. In the case of single cation glasses, the band is broader and more intense. It is almost disappeared in the presence of both alkalis in equal proportion W-O-W.

- A band centered at 753 cm^{-1} is attributed to the symmetric stretching frequency of the P-O-P bridge. In the case of single cation glasses, the band is broader and more intense.

2nd domain: of 900 à 1300 cm^{-1}

- The band centred at 914 cm^{-1}, is attributed to the antisymmetric stretching frequency of the P-O-P bridge. It becomes less wide and less intense in the presence of the two alkalis in equal proportion.

The difference Δυ between the bridge frequencies is 161 cm^{-1}, which indicates a P-O-P angle less than 120°, i.e. a strongly bent pyro group.

This band assignment is unlikely for two reasons:

The composition, established by chemical analysis, is indeed that of a pyro compound; however, this argument cannot be considered decisive, because a small number of compounds are known that are chemically ortho, but structurally pyro.

- The band centered at 1089 cm^{-1}, is attributed to the antisymmetric stretching frequency of the PO_2 bridge. It becomes wider and more intense in the presence of the two alkalis in equal proportion.

- The two bands at 1144 and 1223 cm^{-1} are respectively attributed to the symmetric and antisymmetric valence mode of the groups PO_3. They become less wide and less intense in the presence of the two alkalis in equal proportion.

The mixed alkali effect in glasses xNaI-(0.5-x)Li_2O-0.125WO_3-0.375P_2O_5 is accompanied by a variation in the width and intensity of the IR bands. It should be noted that as the mixed alkali content increases, the intensity and width of the band related to the υ_{POP} vibration increase. This is consistent with the effect of mixed alkali on the vitreous framework. We also note a widening of the band located in the vicinity of 1020 cm^{-1} when the two alkali oxides become approximately in equal proportions, this broadening is, probably, linked to the increase in the number of groups PO_3 distributed in the vitreous network. The IR vibrational study of the glasses of the system xNaI-(0.5-x)Li_2O-0.125WO_3-0.375P_2O_5 allowed us to confirm the alkaline modifier character and the presence of the mixed alkali effect. The IR spectra confirm that these are glasses of overall pyrophosphate composition.

4 Conclusion

This work studies mixed alkali glasses to explore charge transport and structure. The glasses were made using rapid tempering, and their chemical nature was confirmed by ATD and X-ray diffraction.

To determine the conduction mechanism and avoid electrode polarization in solid electrolytes, we used the complex modulus formalism. Results suggest ionic transport occurs through a hopping mechanism, with significant coupling between charge carriers:

- The conductivity σ_{dc} passes through a pronounced minimum when the Li_2O and NaI are present in approximately equal proportion in the glass system xNaI-(0.5-x)Li_2O-0.125WO_3-0.375P_2O_5.

- The activation energy $E_{a\sigma}$ and pre-exponential term σ_0 pass through a pronounced maximum when the Li_2O and NaI are present in approximately equal proportions in the glassy system xNaI-(0.5-x)Li_2O-0.125WO_3-0.375P_2O_5.

- The activation energies $E_{a\sigma}$ and E_{af} determined from the impedance spectra are very close, meaning that

the ionic transport in the glassy system studied is due to a hopping mechanism.

In the IR spectra of glasses xNaI-(0.5-x)Li_2O-0.125WO_3-0.375P_2O_5, These are pyrophosphate glasses, so we observe that the lithium coordination is LiO_4 These results are consistent with the results of J. Swenson [5].

In the glasses xNaI-(0.5-x)Li_2O-0.125WO_3-0.375P_2O_5, tungsten has two types of coordination WO_4 (dominant) and WO_6. For phosphorus, glasses xNaI-(0.5-x)Li_2O-0.125WO_3-0.375P_2O_5 of overall composition orthophosphate (O/P=4) present the two pyrophosphate (dominant) and orthophosphate groups confirmed by IR spectroscopy.

Based on the performed IR spectral investigations, a hypothesis regarding the formation of the vitreous network in the Quaternary system xNaI-(0.5-x)Li_2O-0.125WO_3-0.375P_2O_5 is proposed. The existence of several structural units WO_4, WO_6, PO_4, P_2O_7, LiO_4 is proven, the fraction of the first four units remains constant while that of LiO_4 changes according to the composition of the corresponding glass. The mixed alkali effect in glasses xNaI-(0.5-x)Li_2O-0.125WO_3-0.375P_2O_5 is accompanied by a variation in the width and intensity of the IR bands. It should be noted that as the mixed alkali content increases, the intensity and width of the band relative to the ν_{POP} vibration increase. This is consistent with the effect of mixed alkali on the glass framework P_2O_5-WO_3.

5 References

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