Mixed cation and mixed anion effects in sodium sulphate and lithium-tungsten- phosphorus oxides glasses

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Abstract. The density, activation energies, and electrical conductivity of ionic conductive glasses containing $xNaSO_4$-$(0.5-x)Li_2O$-$0.125WO_3$-$0.375P_2O_5$ based on molar fractions (x = 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50 % mol). Densities vary linearly with the content of Na_2SO_4. The relationship between temperature and total conductivity was analysed using the Arrhenius equation. A set of parallel lines was observed, which means that the electronic and ionic conductivities of these glasses follow Arrhenius' law on the one hand, and on the other hand, that their activation energies are very close. The evolution of the relaxation time τ_σ, and electrical conductivity σ_{dc}, pre-exponential term σ_0, activation energies $E_{a\sigma}$ and E_{af} and frequency f_0 depending on content in Na_2SO_4 does not vary linearly and passes through a pronounced minimum or maximum in the glasses studied therein. This phenomenon is due to the mixed cation exchange effect (MCE) and/or mixed anion exchange effect MAE. These effects in these glasses can be explained using the rigidity theory developed by Phillips and Gupta.

Introduction

The combined mixed modifier effect in glass results in non-linear characteristics due to the mixing of two alkalis, leading to an increase in the hardness of the glass network. This rigidity is caused by the interaction between two ions of different sizes, which limits their movement, thereby obstructing the transition points. Alkali cations alter the properties of glass, particularly when a second monovalent cation is added to a binary alkali glass or when the glass contains divalent cations. This effect, documented since the 19th century [1], stems from Zachariasen's hypothesis, which postulates that oxidised glasses are composed of a fundamental network of covalent bonds, interspersed with non-bridging oxygen ions and modifying cations. The mixed cation effect is observed in various ion pairs, such as alkali and alkaline earth ions. Several models, including that of Lengyel and Boksay [2], have been developed to explain variations in glass characteristics, particularly the phenomenon of blocking in mixed cation glasses. This model indicates that a large ion, due to its low probability of migrating to an unoccupied site, can cause an obstruction in the diffusion pathways of smaller, faster ions, which would slow down the alkali metals. Reducing the diffusion rate leads to a decrease in electrical conductivity in the glass.

The rigidity theory predicts the evolution of various properties of glasses, including the mixed cation effect, taking into account their composition [3-4]. Its expression, incorporating an interaction parameter γ, is explained in the references [3-4]. We incorporate the impact of mixed modifiers into the theory of rigidity, then apply this extension for simplified prediction of the properties of the glasses studied. The mixed cation effect is influenced by two simultaneous contributions: the binding constraints on the modifiers become more or less stringent with the variation of γ. A reduction in γ indicates easier migration of alkali ions, resulting in constant adjustments to the lattice in response to deformations. Migration becomes more complex as the size gap increases, particularly for smaller ions, where the dynamics of larger ions slow down their movement, thereby increasing γ. A size difference exceeding a critical threshold may indicate steric hindrance, affecting the MoO_3-P_2O_5 glass structure during deformation.
Properties related to ionic mobility, such as electrical conductivity, ionic diffusion, dielectric relaxation, and internal friction, as well as glass transition temperature and thermal expansion coefficient, show the most pronounced nonlinear dependence in mixed cation and/or mixed anion glasses [5]. In most of the examined glasses, density, refractive index, microhardness, and ultraviolet and visible transmission show only minor

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deviations from linearity [6-8]. Research on phosphate-based glasses highlights the insufficient investigation of mixed cations and/or mixed anions compared to silicate glasses. This study aims to explore the effects of these mixed components using structural, and electrical characterizations.

Due to their superior chemical durability [9], the focus was on specific glass systems, employing a total content of 50% Na_2SO_4 and Li_2O. This rate was limited to mitigate hygroscopic effects, despite the potential benefits of higher concentrations for observing mixed cation and anion effects. WO_3 was incorporated as a third element, contributing to the creation of thermally stable glasses alongside alkalis and phosphorus oxide, functioning as both a former and modifier oxide. This work will investigate the effects of mixed cations and/or mixed anions on various properties of the glass system, including activation energy, density, and ionic conductivity.

Experimental procedures

The glasses of the aforementioned system are produced following a specific reaction:

$$(0.5\text{-}x)Li_2CO_3 + xNa_2SO_4 + 0.125WO_3 + 0.75(NH_4)H_2PO_4 \rightarrow xNa_2SO_4\ (0.5\text{-}x)Li_2O\ 0.125WO_3\ 0.375P_2O_5 + 0.75NH_3 + 1.125H_2O + 0.5CO_2 \quad (Eq.\ 1)$$

Where x = 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50 % mol. Appropriate quantities of Li_2CO_3, Na_2SO_4, WO_3 and $NH_4H_2PO_4$ are ground and incorporated in a mortar. A muffle furnace is used to combine all quantities in an open platinum crucible. The mixture is then subjected to two heat treatments. The first treatment is at 533 K, which causes the ammonium phosphate to decompose, moisture to be removed and CO_2 to be released. The second treatment is at 1173 K, which allows the reaction mixture to fuse. Finally, the glass is obtained by air quenching.

Analysing the impedance measurements at frequency from 20 to 1 MHz and temperatures from 298 to 533 K, we found the electrical measurements in all the compounds that were studied.

Results and discussion

Density and molar volume

Figure 1 shows the relationship between changes in density and molar volume relative to the cationic ratio in the specified glass system.

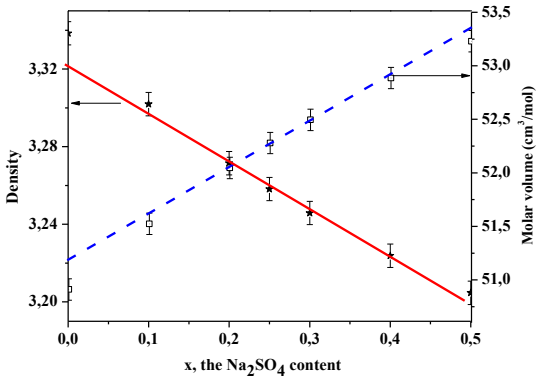
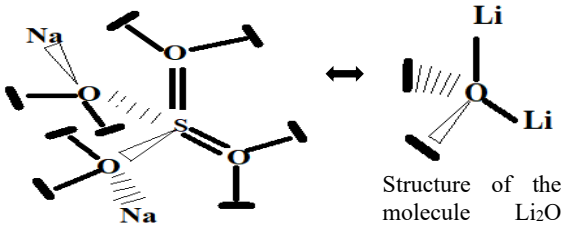


Fig. 1. Density and molar volume variation against of cationic ratio in the glass system mentioned above

The density of glass is closely linked to its composition [10], particularly the Na_2SO_4 content, which causes a linear decrease in density due to its lower molecular weight compared to Li_2O, influencing the glass network's growth.

The molar volume behaviour shows a linear decrease when Li_2O is replaced with Na_2SO_4 in the glass matrix containing fixed amounts of P_2O_4 and WO_3. This change alters the oxygen/tungsten + phosphorus ratio, significantly affecting the proportions of PO_4 and WO_n units. The decrease in V_m is attributed to a reduction in the glass's free volume. The larger volume of the Na_2SO_4 molecule compared to Li_2O contributes to the observed increase in molar volume as represented in the Gillispie figures (figure 2):



Structure of the molecule Na_2SO_4 according to VSEPR

Structure of the molecule Li_2O according to VSEPR

Fig. 2.

IR spectra

Nevertheless, research has analysed phosphate glass materials using infrared spectroscopy [11-12], with the aim of understanding the types of infrared absorption observed, rather than reproducing the exact compositions. Figure (3) shows the IR spectra of the glass system studied, obtained at room temperature between 400 and 4000 cm^{-1}.

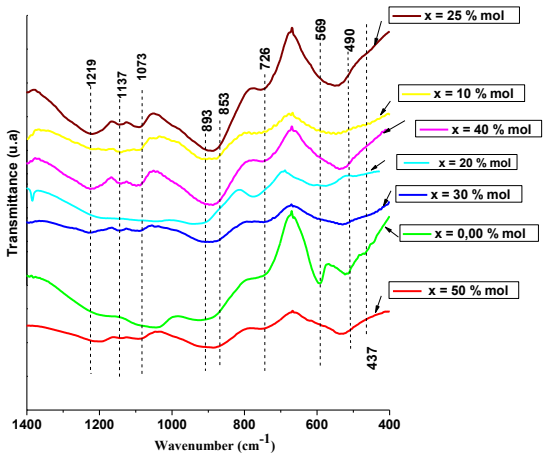


Fig. 3. Infrared Spectra in the glass systems mentioned above

The general characteristics of the spectra of the glasses in the glass system mentioned above are briefly presented:

- The existence of a strong mode at 569 cm^{-1}, attributed to the deformation of phosphate groups, is noted, with a possible contribution from LiO_4 and WO_4. This mode exhibits a minimum for the mixed mobile ion glass with a composition of x = 30% mol.
- A low-intensity mode at 632 cm^{-1} is related to the W-O-W symmetric stretching. Single-cation glasses exhibit greater intensity and mode width, while mixed-cation glass with a composition of x = 30% mol is almost absent.
- The symmetric stretching frequency of the P-O-P bridge is 726 cm^{-1}, with broader and more intense modes for glasses containing a single Na or Li cation.
- The antisymmetric stretching frequency of the P-O-P bridge is 893 cm^{-1}, and it decreases and attenuates in the mixed mobile ion glass with composition x = 30% mol. The $\Delta\upsilon$ difference of 167 cm^{-1} indicates a P-O-P angle of less than 120°, suggesting a strongly bent pyro group. This attribution of modes is questionable because, although chemical analysis has revealed the composition of a pyro compound, this is not conclusive, as some compounds are chemically ortho while having a pyro structure.
- The mode centred at 1073 cm^{-1} corresponds to the antisymmetric stretching frequency of the PO_2 bridge, broadening and intensifying for the mixed mobile ion glass with composition x = 30% mol.
- The symmetric and antisymmetric valence vibrations of the PO_3 groups are attributed to the modes at 1137 and 1219 cm^{-1} respectively. In the mixed mobile ion glass with a composition of x = 30% mol, these modes show a reduction in width and intensity.

In the glass system studied, the effect of mixed cations and/or anions induces changes in infrared vibration modes, particularly the intensity and width of the υ_{POP} vibration mode, which increase with the concentration of mixed cations and/or anions. An expansion of the mode around 1037 cm^{-1} is observed for a mobile ion glass with a composition of x = 30% mol, probably related to the increase in PO_3 groups in the matrix. Infrared analysis confirmed the impact of Na^+ and Li^+ cations on the structure of the glass network, indicating that these glasses have a pyrophosphate composition.

Complex impedance spectroscopies

1.1.1 Direct current conductivity σ_{dc}

The glasses mentioned were subjected to conductivity measurements from 298 to 533 K, revealing ionic conductivity σ_{dc} graphs that follow an Arrhenius law with similar activation energies (figure 4).

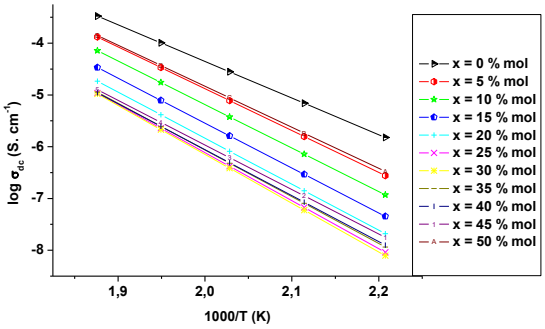


Fig. 4. Change of electric conductivity versus 1/T in the glass system mentioned above.

In order to highlight the impact of mixed cations and/or mixed anions, we have created a graph showing $\log_{10}(\sigma_{dc})$ as a function of f(x) at various temperatures. Figure (5) illustrates the conductivity σ_{dc} in relation to the cationic ratio of the glass system mentioned above. The conductivity σ_{dc} of glasses at 453 K decreases from 17.78×10^{-7} S cm^{-1} for Li-only alkali glass to 3.16×10^{-7} S cm^{-1} for Na-only alkali glass, and reaches 0.1×10^{-7} S cm^{-1} for Li-Na mixed alkali glass. The incorporation of alkali ions reduces conductivity and causes a significant deviation from linearity for mixed cation glasses, illustrating the effect of mixed cations on the electrical characteristics of the samples analysed.

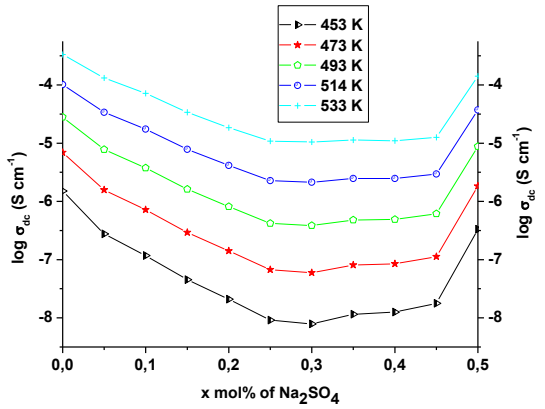


Fig. 5. dc conductivity variation against of cationic ratio in the glass system mentioned above.

1.1.2 Activation energies $E_{a\sigma}$ and $E_{a\tau}$

It is possible to determine the activation energies $E_{a\sigma}$, $E_{a\tau}$, the frequency f_0 and the pre-exponential terms σ_0 from figure (4). Figure (6) shows that these four

parameters ($E_{a\sigma}$, $E_{a\tau}$, f_0 and σ_0) reach a maximum for a mixed mobile ion glass with a composition of x = 30% mol.

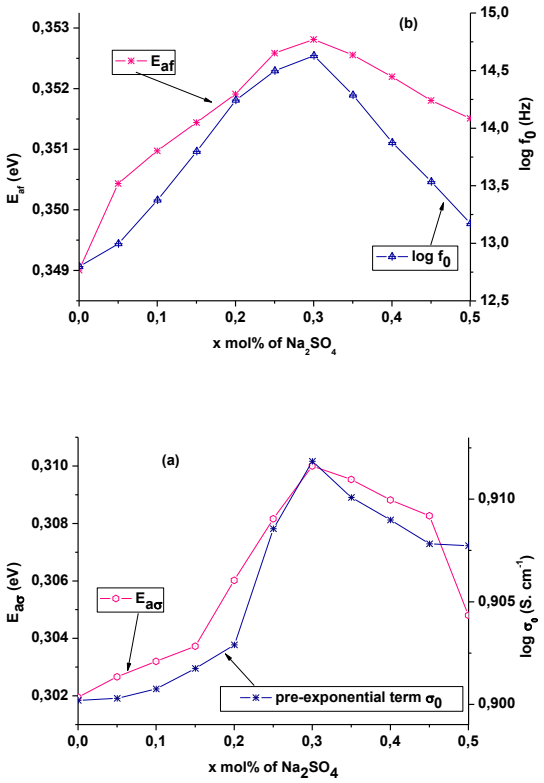


Fig. 6. Activation energies $E_{a\sigma}$, σ_{af} , Frequency f_0 and pre-exponential term σ_0 evolution against of cationic ratio in the glass system mentioned above.

Glass with a composition of x = 30% mol exhibits low ionic mobility. Single-cation and mixed-cation glasses exhibit similar characteristics, such as increased ionic conductivity σ_{dc} and reduced activation energies proportional to the mobile cation. Lithium glasses have higher conductivity than sodium glasses of equivalent composition, due to their higher ionic mobility. The variation in conductivity with respect to the molar fraction of alkali is not linear. This means that not all lithium and sodium cations are in motion, with some ions contributing to the structure while others remain mobile. The association of these cations with oxygen atoms not bonded to phosphorus in highly charged glasses influences their mobility, with ions associated with phosphate groups being the most mobile. It is also mentioned that mixed cation glass with a composition of x = 30% mol has the lowest conductivity, attributed to a decrease in the mobility of the modifying cations. This is interpreted via the rigidity theory, suggesting that energetically unfavourable sites may form near certain cations. The results are consistent with previous studies conducted by Rodrigues et al [4]. It is proposed that the mixed alkali effect results from changes in the coordination and interaction of modifying agents, where an increase in the concentration of one category of alkali ions increases their mobility, while that of the other category of ions decreases due to its reduced concentration.

1.1.2 Alternating current conductivity σ_{ac}

The conductivity σ_{ac} increases with frequency, as illustrated in Figure (7) for a specific composition.

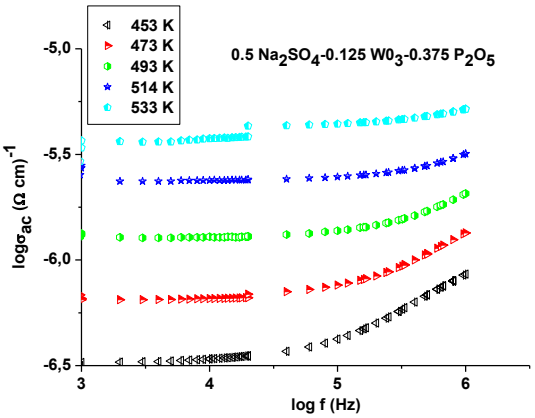


Fig. 7. The ac conductivity of the glass $0.5Na_2SO_4$-$0.125WO_3$-$0.375P_2O_5$

The decrease in the total concentration of mobile ions reduces the effect of mixed cations and/or anions [13]. Furthermore, the effect of mixed alkalis is reduced when the two types of mixed alkalis have similar ionic radii.

1.1.3 Dielectric relaxations: frequency response

Figure (8) also shows the normalised imaginary part M''/M''_{max} for mixed and single mobile ion glasses at various temperatures. At a specific temperature, these spectra exhibit asymmetric peaks located approximately in the dispersion zone of M*.

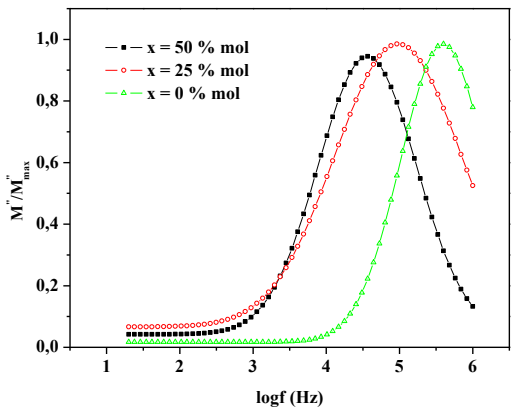


Fig. 8. Frequency dependence of the M"/M"$_{max}$. for the two single alkalis and mixed alkali glasses.

At the limit of M", a natural frequency f_p manifests itself. To the left of the peak, the frequency domain concerns the extended movements of mobile ions, while to the right, it concerns ions confined to their potential wells. The peak in the reduced frequency range indicates the transition from short-range mobility to long-range mobility [14]. The relationship $\omega\tau_\sigma$=1 indicates that τ_σ, the most probable conductivity relaxation time [15], is established quantitatively. As the temperature increases, the maxima of the asymmetric peaks of M" shift towards

higher frequencies [16]. Both before and after the frequency peak, the M''/M''$_{max}$ graphs show non-exponential relaxation behaviour of the conductivity, with a half-width at half-height of the peak much wider than that predicted by the Debye model [16]. Mixed cation glasses have a lower Kohlrausch parameter β value than single cation glasses (Fig. 9).
An Arrhenius-type law is observed for conductivity σ_{dc} and relaxation time versus of temperature, with quasi-parallel straight lines suggesting similar activation energies $E_{a\sigma}$ and $E_{a\tau}$. This indicates that ion transport in the glass system mentioned above results from a "hopping" mechanism [15].

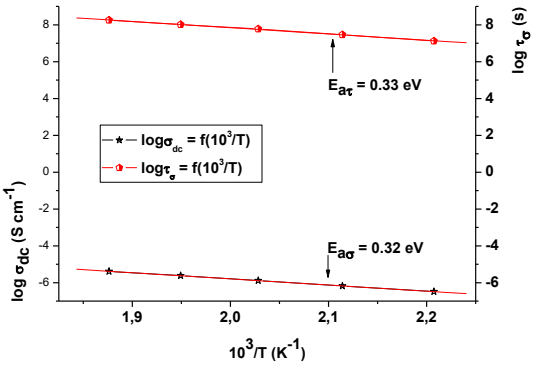


Fig. 9. Variation in conductivity log(σ_{dc}) and relaxation time log(τ_σ) in the glass system mentioned above with temperature.

The conductivity σ_{dc} decreases when Li_2O is partially replaced by Na_2SO_4 in the glasses, which is consistent with previous work [17]. This phenomenon explains why the interaction between sodium and lithium ion mobility leads to a minimum in conductivity σ_{dc}, which depends on ion concentration. This minimum could result from a variation in the interaction parameter γ of alkali ions, as the emission of an ion decreases when it is replaced by another. A convergence points forms when the interaction parameters γ of these ions become identical, making electrical transport essentially dominated by the most mobile ion on each side of the crossing point [4]. Semi-quantitative theories have been proposed to explain the effect of mixed cations and/or anions, but none covers the subject exhaustively. These theories link the decrease in conductivity to differences in coordination and interactions between Na_2SO_4 and Li_2O modifiers. Tomozawa and his team [18] established that the high static dielectric constant of mixed alkali glasses stems from the negative enthalpy of alkali ions. Ingram and colleagues [13] developed a diffusion model based on percolation, where the enthalpy of two types of alkali ions is negative. Bunde and his team [19] explained the decrease in conductivity in these glasses by low-mobility complexes, also due to negative mixing enthalpy. In contrast, the study by Maass et al. [18] showed that alkali ions establish and maintain their specific environment, leading to positive enthalpy between different categories of ions. These results suggest the existence of mobile ions forming their own environments, which forms the basis of a unified model of site relaxation, combining jump relaxation and structural dynamics models.

Research conducted over the past 30 years on the effect of mixed cations and/or mixed anions has established that its structural basis is explained by the dynamic structure model (DSM) developed by Bunde et al [13,19]. Here is a presentation of the DSM model: in a mono-cationic glass, cations such as Li occupy positions suited to their needs, without requiring major rearrangements of the glass network. The addition of a second cation, such as Na, creates two distinct types of modifier sites. Cations can migrate between similar sites, and it is also possible to perform transfers between different sites when the Li/Na ratio is close to unity.
Ingram et al. [15] assert that the displacement of cations to different sites causes a reconfiguration of the lattice in order to minimize the distortions caused by a Li atom at an Na site (or vice versa). When cations are statistically distributed in the glass structure, it is expected that a Li/Na molar ratio of one maximizes the probability of modifiers occupying different sites, resulting in increased flexibility of the glass network and often a reduced glass transition temperature for compositions near or equal to Li/Na = 1.
The low conductivity of mixed cation glass is explained by the distribution of free volume, which gels during cooling. This free volume influences annealing processes close to T_g, and it is suggested that certain portions are 'captured' by moving ions and incorporated into diffusion paths. Part of the available volume is used to create $\overline{Li}$ and $\overline{Na}$ empty sites, which frees up a volume that circulates around the channels for these ions, slowing down ion transport. The addition of Li^+ cations retains more free volume, thereby reducing availability for Na^+ cations, resulting in minimal mobility for both ions at equal concentrations. For single-cation glasses (x = 0% and x = 50% mol), the mobility of Li^+ and Na^+ ions is due to the high probability of transition. On the other hand, for mixed cation glass (x = 30%), the probability of transition is low, resulting in minimal conductivity σ_{dc}. At high frequencies, ion movement becomes localized, reducing ionic conductivity. The results show a significant dip in σ_{dc} at x = 30% mol, especially at low temperatures, confirming previous scientific research [13,19-20]. The reduction in the effect of mixed cations and/or anions is observed with a decrease in mobile ion concentrations [21]. At very low concentrations, this effect becomes negligible [22]. Single-cation glass exhibits good conduction connectivity, whereas in mixed-cation glass, the diversity of cation sites hinders certain conduction paths, resulting in a significant decrease in ionic mobility.

A new understanding of the mixed cation effect in glass highlights the interaction between cation displacements, where small cations, such as Li^+, take up unoccupied sites of larger cations such as Na^+, which occupy narrower locations. This generates structural interactions that mitigate mechanical stresses, thereby shedding light on several major phenomena. Recently, an ion-matrix interaction approach has been introduced, linking the stress effect to ionic conductivity in mixed cation glasses [23]. This study examines a system of $xLiPO_3$-$(1-x)NaPO_3$ glasses ($0 \leq x \leq 1$), demonstrating a mixed cation effect and a minimum in σ_{dc} and T_g [24].

The activation volume is given by the equation: ΔV^{*}=-RTdlnσ/dP Eq (2) where P is the equilibrium pressure (in Pa).
It can be observed that the activation energy follows similar trends to those of the activation volume, with a distinct peak for mixed ion-mobile glass according to Bandaranayake et al [25]. Thus, the activation energies $E_{a\sigma}$ and $E_{a\tau}$ evolve in a similar manner to the activation volume as a function of the cationic ratio [23]. Large cations, such as Na^{+}, expand the glass structure, while small cations, such as Li^{+}, cause it to contract, which is corroborated by ion exchanges leading to contraction of the network [26]. However, the replacement of Li^{+} ions by Na^{+} ions, which causes expansion, is a mystery in terms of the amount of activation observed. Ultimately, the activation volume of mixed cation glasses is simply an arithmetic sum of those of single alkali glasses: ΔV^{*}(MA glass)$\cong$ ΔV^{*}(First SA glass) + ΔV^{*}(Second SA glass) (Eq. 3)

Conclusion

Experimental results show that the introduction of Na_2SO_4 and Li_2O significantly alters the physical, structural and electrical characteristics of the glasses analysed. The addition of sodium sulphate and lithium oxide transforms the structure and properties of the glass.
- A pronounced minimum in the sigma conductivity index d and relaxation time tau sigma is observed in the analysed glasses when the molar proportion of Na_2SO_4 reaches 30% mol.
- The four parameters ($E_{a\sigma}$, $E_{a\tau}$, f_0 and σ_0) of the analysed glasses reach a significant maximum at 30% mol of x(Na_2SO_4).
- The close activation energies $E_{a\sigma}$ and $E_{a\tau}$ suggest that ion transport in the glass system is due to a hopping mechanism.
In the infrared spectra of the glasses examined, pyrophosphate glasses are analysed. It can also be seen that the lithium coordination is tetrahedral LiO_4. Glasses with an orthophosphate composition (O/P = 4) show, through infrared spectroscopy, the presence of pyrophosphate and orthophosphate groups. A hypothesis on the constitution of the glass network is suggested, indicating the existence of structural units such as WO_4, WO_6, PO_4, P_2O_7 and LiO_4. The proportions of the first units are stable, while that of LiO_4 varies depending on the composition of the glass. The presence of mixed cations and/or anions modifies the IR modes, with an increase in the concentration of mixed cations leading to increased intensity and width of the υ_{POP} vibration mode, consistent with the effect of mixed cations and anions on the P_2O_5-WO_3 glass structure. In the glasses examined, tungsten coordinates mainly in two forms: WO_4, which predominates, and WO_6, in agreement with the results of Swenson et al [27].

References

[1] Ngai KL., & Martin SW., Correlation between activation enthalpy and Kohlrausch's exponent for ionic conductivity in oxide glasses, Physical Review B, 40 (15) (1989) 10550. https://doi.org/10.1103/PhysRevB.40.10550.

[2] Vegiri A., Varsamis C. P., & Kamitsos E. I., Molecular dynamics investigation of mixed-alkali borate glasses: Short-range order structure and alkali-ion environments. Physical Review B-Condensed Matter and Materials Physics, 80(18) (2009) 184202. https://doi.org/10.1016/S0022-3093(02)01560-0.

[3] Tomozawa M., & McGahay V., Mechanism of the mixed alkali effect based upon the thermodynamic state of glass. Journal of non-crystalline solids, 128(1) (1991) 48-56. https://doi.org/10.1016/0022-3093(91)90775-2.

[4] Bunde A., Ingram MD et Russ S., New interpretation of the dynamic structure model of ion transport in molten and solid glasses, Phys. Chem. Chem. Phys. 6 (2004) 3663–3668. Doi :10.1039/B316738K.

[5] Maass P., Towards a theory of the mixed alkaline effect in glass, J. Non Cryst. Solids, 255 (1999) 35–46. Doi :10.1016/S0022-3093(99)00422-6.

[6] Djamel M. (2011). "Alkali mix" effect in Sb_2O_3-M_2O-ZnO glasses: Elastic, mechanical and optical properties (Doctoral dissertation, Université Mohamed Khider–Biskra Faculté des Sciences).

[7] Hamam K. J., & Salman F., Dielectric constant and electrical study of solid-state electrolyte lithium phosphate glasses. Applied Physics A, 125(9) (2019) 621.

[8] Shan Z., Zhang Y., Liu S., Tao H., & Yue Y., Mixed-alkali effect on hardness and indentation-loading behavior of a borate glass system. Journal of Non-Crystalline Solids, 548 (2020)120314. https://doi.org/10.1016/j.jnoncrysol.2020.120314

[9] Ingram MD., Imrie CT. et Konidakis I., Activation and relaxation volumes of sites in mixed alkali glasses, J. Non Cryst. Solids, 352 (2006) 3200–3209. doi:10.1016/j.jnoncrysol.2006.05.009

[10] Bandaranayake PWSK., Imrie CT., and Ingram MD., Pressure-dependent conductivities and activation volumes in LixNa(1-x)PO3 glasses: evidence for a new matrix coupling mechanism in cationic mixed glasses? Phys. Chem. Chem. Phys., 4 (2002) 3209-3213. Doi: 10.1039/b201215d.

[11] Swenson J., Matic A., Brodin A., Börjesson L., & Howells W. S., Structure of mixed alkali phosphate glasses by neutron diffraction and Raman spectroscopy. Physical Review B, 58(17) (1998) 11331. https://doi.org/10.1103/PhysRevB.58.11331.