

# Mixed alkali effect in Li and Na aluminophosphate glasses: influence of the cation environment

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## Abstract

This paper deals with the variation of the mixed alkali effect (MAE) in Li and Na aluminophosphate glasses. The general system investigated is:  $0.46 [x\text{Na}_2\text{O}(1-x)\text{Li}_2\text{O}]$ ,  $0.54 [y\text{Al}_2\text{O}_3(1-y)\text{P}_2\text{O}_5]$ , with  $x$  varying between 0 and 1 to probe the MAE, and  $y$  between 0 and 0.08 to modify the cation environment and to try to understand how the amorphous host affects the ionic motions. We show that the dc conductivity minimum characteristic of the MAE effect decreases and almost disappears as  $\text{Al}_2\text{O}_3$  is added to mixed phosphate glasses. On another hand, the dc conductivity of the single alkali glasses is almost not affected by  $\text{Al}_2\text{O}_3$  addition. Dielectric relaxation characteristics also change with the  $\text{Al}_2\text{O}_3$  concentration in mixed glasses and not in single ones. On another hand, the mixed alkali peak measured using mechanical relaxation appears to be almost not affected by the presence of  $\text{Al}_2\text{O}_3$ . This decoupling between the mechanical and dielectric relaxation processes appears to «through into question» the proposal that the mechanical relaxation in mixed alkali glasses accounts for sites reconfiguration to adapt to the different cations.

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## 1. Introduction

Mixed alkali effect (MAE) is a longstanding subject of investigation in oxide glasses. MAE corresponds to a nonlinear evolution of certain properties with the relative cation concentration in oxide glasses including two dissimilar alkali cations. The ionic conductivity is the most affected property and exhibits an important minimum when the relative cations concentration is approximately equal to 1/2 [1–3]. Interestingly other “dynamical” properties also exhibit a more or less pronounced nonlinearity: internal friction, viscosity and chemical durability, glass transition, expansion coefficient... On another hand, “static” properties, like density for example, appear to be linear [1]. Different models for MAE have been proposed in the

literature and are compiled in several excellent reviews [1–3]. These models assumed either large structural modifications induced by mixing mobile species of different sizes or specific interaction between these dissimilar mobile species. None of these assumptions have been observed experimentally [4,5]. Some years ago, EXAFS data obtained by Greaves et al. [6] indicated that the environment of the mobile cations in glasses is well determined by the type of cation that “creates” the site it occupies. Based on these results, Bunde et al. [7–9] proposed a new model for ionic migration in glasses, called the Dynamic Structure Model (DSM). The main idea of the DSM model is the existence of mismatches between the different types of sites designed by cations in the glass. Ionic migration is associated with a “memory effect” of the sites previously occupied, which leads to the creation of ionic pathways. Further structural [10,11] and computer simulation [12] results confirmed that the environment of the different cation types differ from each other. The DSM explanation of the slowing down of

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the cations dynamics in mixed alkali glasses is associated with the relaxation time required to accommodate sites to cations of different type. The Random Distribution Model (RDM) [13] is based on almost the same arguments. MAE is assumed to be a consequence of the random mixture of ions of different type with different environments, leading to “low-dimensional migration pathways” for each type of alkali. However, this model does not introduce any eventual reorganisation of the sites. The additional mechanical loss observed by Dynamic Mechanical Analyses in glasses containing dissimilar cations has however been assumed by other authors [14–16] to be the experimental proof of the sites reconfiguration [17]. It is indeed not well established if the ionic pathways are “frozen in” below the glass transition temperature, or if the local density fluctuations allow some sites relaxation to accommodate eventually to different type of cation. There is still an important debate on these questions and more generally on the origin of MAE.

In this study, we try to probe the eventuality of a site relaxation associated with the MAE. Site relaxation implies a local network reconfiguration to accommodate sites to cations of different type. In order to test this eventual local cooperativity between mobile cation and network, we analysed the MAE in three series of mixed alkali aluminophosphate glasses with all the same global alkali content, but with a different alumina to phosphorus ratio. The general system investigated is:  $0.46 [x\text{Na}_2\text{O}(1-x)\text{Li}_2\text{O}]$ ,  $0.54 [y\text{Al}_2\text{O}_3(1-y)\text{P}_2\text{O}_5]$ . The three series correspond to  $y=0, 0.04$  and  $0.08$ , and in each series, five glasses were synthesised ( $x=0, 0.25, 0.5, 0.75$  and  $1$ ). Structural analyses of these glasses have been performed by RMN, SAXS, and WAXS and will be presented in another paper [18]. In this paper, we focus on the dynamical properties of these systems, and more specifically on the sub- $T_g$  relaxation processes associated with the MAE. These relaxation processes are probed both by mechanical and dielectric spectroscopy.

## 2. Experimental procedure

Fifteen lithium and sodium aluminophosphate glasses (see Table 1 for detailed composition) were prepared from adequate mixture of reagent-grade  $\text{Al}(\text{OH})_3$ ,  $\text{Li}_3\text{PO}_4$ ,  $\text{H}_2\text{NaPO}_4$ , and  $\text{H}_2(\text{NH})_4\text{PO}_4$ , melted in air in platinum crucibles. Glasses were then cast into steel mold and reheated for 1 h just above  $T_g$ . Cooling down was performed for all glasses at the same rate ( $0.5\text{ }^\circ\text{C}/\text{min}$ ) up to  $100\text{ }^\circ\text{C}$ , and the obtained samples were then stored under dry conditions to prevent hydration. Glass transition temperature ( $T_g$ ) of each glass was determined using Differential Scanning Calorimetry (Setaram TG/DSC Labsys-1600) at a heating rate of  $5\text{ K}/\text{min}$ .

The dynamic mechanical measurements were performed using a Perkin Elmer Dynamic Mechanical Analyser (DMA

Table 1

Composition of the  $\text{Na}_2\text{O}-\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5$  glasses synthesized and analysed in this study

Glasses composition	%Na <sub>2</sub> O	%Li <sub>2</sub> O	%P <sub>2</sub> O <sub>5</sub>	%Al <sub>2</sub> O <sub>3</sub>
Li <sub>46</sub> P <sub>54</sub>	0	46	54	0
Na <sub>11.5</sub> Li <sub>34.5</sub> P <sub>54</sub>	11,5	34,5	54	0
Na <sub>23</sub> Li <sub>23</sub> P <sub>54</sub>	23	23	54	0
Na <sub>34.5</sub> Li <sub>11.5</sub> P <sub>54</sub>	34,5	11,5	54	0
Na <sub>46</sub> P <sub>54</sub>	46	0	54	0
Li <sub>46</sub> Al <sub>4</sub> P <sub>50</sub>	0	46	50	4
Na <sub>11.5</sub> Li <sub>34.5</sub> Al <sub>4</sub> P <sub>50</sub>	11,5	34,5	50	4
Na <sub>23</sub> Li <sub>23</sub> Al <sub>4</sub> P <sub>50</sub>	23	23	50	4
Na <sub>34.5</sub> Li <sub>11.5</sub> Al <sub>4</sub> P <sub>50</sub>	34,5	11,5	50	4
Na <sub>46</sub> Al <sub>4</sub> P <sub>50</sub>	46	0	50	4
Li <sub>46</sub> Al <sub>8</sub> P <sub>46</sub>	0	46	46	8
Na <sub>11.5</sub> Li <sub>34.5</sub> Al <sub>8</sub> P <sub>46</sub>	11,5	34,5	46	8
Na <sub>23</sub> Li <sub>23</sub> Al <sub>8</sub> P <sub>46</sub>	23	23	46	8
Na <sub>34.5</sub> Li <sub>11.5</sub> Al <sub>8</sub> P <sub>46</sub>	34,5	11,5	46	8
Na <sub>46</sub> Al <sub>8</sub> P <sub>46</sub>	46	0	46	8

7). The loss  $E''$  and the storage  $E'$  moduli were determined using a standard three points bending configuration. The sample dimensions were  $20 \times 2 \times 1\text{ mm}^3$ . The samples were perturbed at a fixed frequency (between 0.1 and 10 Hz) and temperature was increased at a typical rate of  $3\text{ }^\circ\text{C}/\text{min}$ .

A HP4192A impedance analyser was used to analyse dielectric response of 2-mm-thick samples mounted between brass electrodes. Measurements were performed at fixed temperatures (controlled within  $\pm 2\text{ }^\circ\text{C}$ , from room temperature up to  $240\text{ }^\circ\text{C}$ ) and increasing the frequency from  $10^{-2}$  to  $10^6\text{ Hz}$ . To determine the direct conductivity, samples were coated with gold to obtain non-blocking electrodes. The dc conductivity is obtained by extrapolating the plateau at low frequency, on the typical spectra of the real part of the conductivity  $\sigma'$  versus frequency logarithm (not shown here). To focus on relaxation processes, a thin teflon film is imposed between the sample and the electrodes, in order to obtain blocking electrodes. Dielectric relaxation caused by the transient conductivity is then directly distinguishable and will be analysed in term of modulus, as explained later.

## 3. Results

The aluminophosphate glasses that we synthesized and analysed can be classified in three different series corresponding respectively to  $y=0, 4$  and  $8\text{ mol}\%$   $\text{Al}_2\text{O}_3$ . In each series, the relative alkali ratio  $\text{Na}/(\text{Na}+\text{Li})$  varies between 0 and 1 (0, 0.25, 0.5, 0.75 and 1) allowing to probe the mixed alkali effect. This MAE is shown in Fig. 1. The isothermal dc conductivity ( $373\text{ K}$ ) plotted as a function of the relative alkali ratio exhibits a minimum around 0.5, as usually observed. A more interesting observation is that the magnitude of the mixed alkali effect (corresponding to the departure from additivity in dc conductivity) evolves with  $\text{Al}_2\text{O}_3$  content. It almost disappears for  $8\text{ mol}\%$   $\text{Al}_2\text{O}_3$  glasses, when it approaches 4 orders of magnitude of 0

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