ESRF	Small angle x-ray scattering in mixed alkali aluminophosphate glasses	**Experiment number:** 02 01 112
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Report:

We investigate the structure of $(Na_2O)_{46x}(Li_2O)_{46(1-x)}(P_2O_5)_{54-y}(Al_2O_3)_y$ glasses with different x varying from 0 to 1 and y=0, 4 or 8. The aim of this work is to study the relationship of the structure and the nature of the network (the ratio P/Al) with the ionic mobility. The latter is discussed in terms of the so-called "mixed-alkali" effect *i.e.* a non-linear variation of some physical properties with the concentration in one alkali when the total amount of alkali is constant. The structure is also investigated by RMN measurements and wide angle X-ray scattering.

We have performed SAXS measurements at room temperature in the 0.02-1.2 $Å^{-1}$ range for 15 samples corresponding to x=0; 0.25; 0.5; 0.75 and 1. We can observe in figure 1 that the scattering intensity for samples without aluminum is flat (slightly decreasing with q) in the 0.1-0.8 $Å^{-1}$ range, *i.e.* we observe no heterogeneity regions. The signal can be fitted to $I(q=0)\exp(-bq^2)$ law (eq. 1) in the 0.4-0.8$Å^{-1}$ range and the scattered intensity is independent of the nature of the alkali (Na or Li). This analysis is consistent with scattering due to density fluctuations. On the other hand, the scattering of glasses with 4 or 8% aluminum (see figure 2 for y=8) exhibit a well defined peak in the low q region, due to heterogeneity regions. The position of this peak vary with the aluminum content: around q=0.2 $Å^{-1}$ for y=8 and q=0.15 $Å^{-1}$ for y=4, so that it is related to distances around 30-40 Å involving Al atoms. The distance vary approximately like the square root of the concentration, in agreement with a homogeneous distribution of Al atoms. One can note on figure 2 that the intensity of the heterogeneity peak present a mixed alkali effect.

In addition, temperature dependent measurements have been performed in 4 different glasses : 1 without Al and 4 with Al. Two examples are shown on figure 3 and 4. As stated below, in the case of glasses without Al (see fig. 3), the signal below q=0.8

Å^{-2} can be attributed to fluctuations and can be extrapolated to $q = 0$ using eq. 1. The resulting $I(q = 0)$ is shown on the inset of figure 3 as a function of temperature. One can observe two regimes : a slow increase with temperature in the glassy state and a steeper increase above the glass transition, as already observed in silicates glasses [1]. In glasses with aluminum, when the temperature increases, the heterogeneity peak shift towards lower q value, indicating that the size of the heterogeneity regions increase. The intensity in the peak region at q=0.16 Å^{-1} first increases, suggesting that the quantity of heterogeneity regions, and then decreases, which can be due to a broadening or to the shift to smaller q. The analysis of the density fluctuations using eq. 1 is more difficult because the extrapolation can be performed only in a short q-range, or after quantitative analysis and subtraction of the heterogeneity peak. However the intensity as a function of temperature at a q value around 1 Å^{-1}, in the region where density fluctuations dominates yield a curve similar to the inset of fig. 3. The results about the influence of Al on the structure are now to be discussed in relationship with the dynamics and with other structural data.

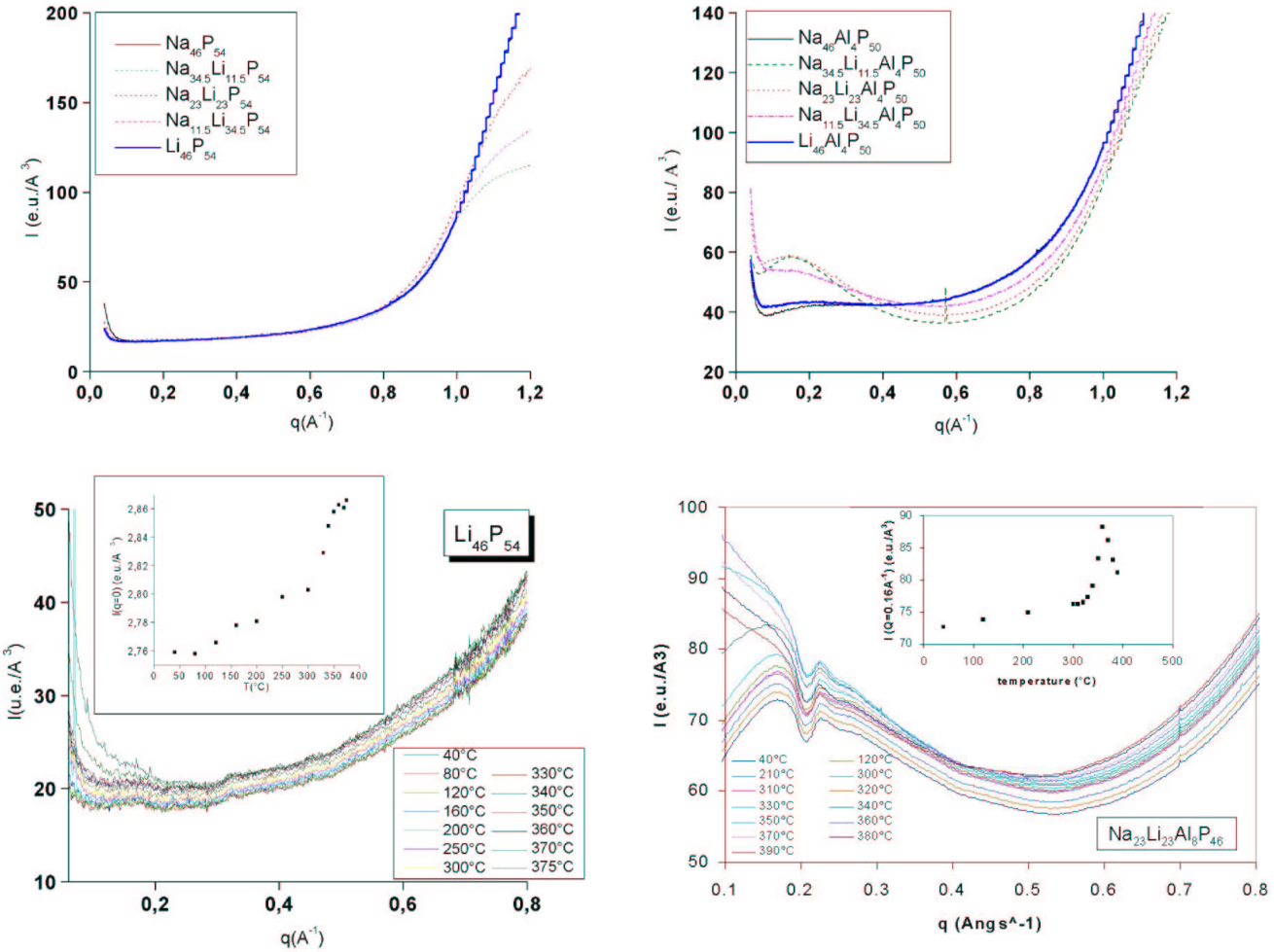

Fig. 1(top, left): SAXS intensity for five glasses without Al. Fig. 2(top, right): SAXS intensity for five glasses with 4% Al. Fig. 3 (bottom, left): SAXS intensity as a fonction of temperature for one glass without Al. Inset: I(q=0) as a function of temperature. Fig. 4 (bot., right): SAXS intensity as a fonction of temperature for one glass with 8%Al. The intensity decreases around q=0.2 Å^{-1} is due to imperfection in subtracting the empty cell. The inset show the intensity as a function of the temperature in the region of the heterogenity peak.

[1] C. Levelut, A. Faivre, R. Le Parc, B. Champagnon, J.-L. Hazemann, L. David, C. Rochas, J.-P. Simon, Journal of Non-cryst. Solids 307-310 (2002) 426-435.