ESRF	**Experiment title:** Studies on atomic dynamics in silicate glasses with aXPCS	**Experiment number**: HC-3159
Beamline: ID10	**Date of experiment**: from: 26.04.2017 to: 02.05.2017	**Date of report**: 29.08.2017
Shifts: 18	**Local contact(s)**: Federico Zontone	*Received at ESRF:*

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Report:

We proposed to study atomic diffusion in silicate glasses. In the past, aXPCS was shown to be an important tool to study atomic diffusion in crystals as well as in glasses [1]. We proposed to extend the studies to alkali silicate glasses, which are one of the most thoroughly studied glassy materials in terms of their structure [2]. Small-angle scattering studies of our own group (unpublished) show that in our alkali silicate samples no inhomogeneities on the mesoscopic length scale exist. We expect therefore only one (jump) diffusion mechanism at work compared to lead silicate, where it was shown, that the inhomogeneities can play an important role.

For this beamtime we prepared different alkali silicates as thin plates such as 15(Na_2O) 85(SiO_2), 40(Na_2O) 60(SiO_2), 10(Rb_2O) 90(SiO_2), 15(Rb_2O) 85(SiO_2) and a mixed alkali oxide sample 15(Li_2O) 15(Rb_2O) 70(SiO_2) using the common procedure [1]. The samples were characterized by means of SAXS, X-ray transmission measurements, Differential Scanning Calorimetry and density measurements.

However, since our proposal have been written, an unexpected development in the field of Atomic-Scale X-ray Photon Correlation Spectroscopy took place. It was found by Ruta et al. [3] that X-rays used to study diffusion in materials by means of aXPCS induces dynamics in some of the investigated samples (SiO_2, GeO_2). This effect has been considered earlier, see Leitner et al. [4], but was not confirmed within experimental errors in $Cu_{90}Au_{10}$ intermetallic crystal. Also the metallic glass $Zr_{65}Cu_{27.5}Al_{7.5}$ investigated by Ruta et al [3] showed no beam induced effects.

Since SiO_2 is the glass forming component of the glasses which we proposed to study, it was imperative to check this effect in our samples. We also checked the flux dependency in the previously investigated lead silicate glasses, namely in 30(PbO)70(SiO_2). We recorded the q-dependence for some alkali silicates like 15(Rb_2O) 85(SiO_2) showing a non-trivial behaviour at large wave vector transfers.

The experimental set-up was as follows: a home-made vacuum furnace with the option of resistive heating was used. A beam energy of 8.1 keV and an ANDOR CCD Camera was used to record the speckle patterns during the experiment. For some measurements the furnace was heated up to a maximal temperature of 530°C. Typical illumination times were 3-5 seconds and the contrast factor for XPCS was between a few percent for alkali silicates and well beyond 10% for lead silicates.

All investigated samples have shown a flux dependency of the atomic dynamics with a different magnitude (slope of the linear dependence on the inverse flux), see Fig. 1(a).

At certain times structural scans were performed to monitor the possibility of structural changes (i.e. beam damage). Beam damage was observed in some samples like $15(Rb_2O)85(SiO_2)$, where the first sharp diffraction peak (glass peak) slightly decreased in intensity. By increasing the temperature a subsequent healing effect was observed. See Fig. 1(b).

The lead silicate sample $30(PbO)70(SiO_2)$ equilibrated for a long time after each temperature change. We checked for the temperature dependence of the beam-induced dynamics and our preliminary results indicate that the effect becomes weaker going closer to the glass transition temperature but never terminates. In our opinion it is the most interesting result of our beamtime and it infers far-reaching consequences for studies of dynamics with XPCS methods.

This work is supported by the Austrian Science Fund (FWF): P28232-N36.

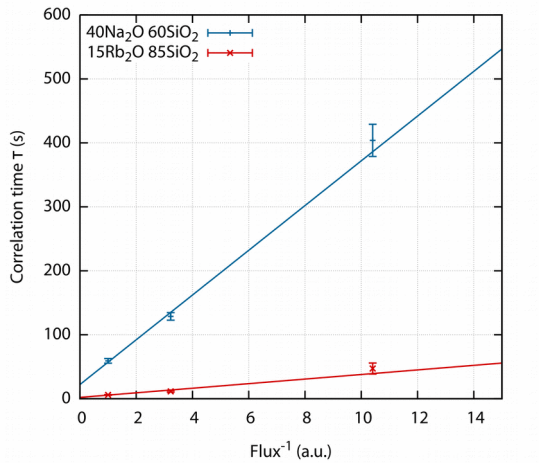

Figure 1(a): Relationship between correlation times and inverse flux. Both measurements were at room temperature at q=17 nm^{-1} (maximum of the first peak in the structure factor)

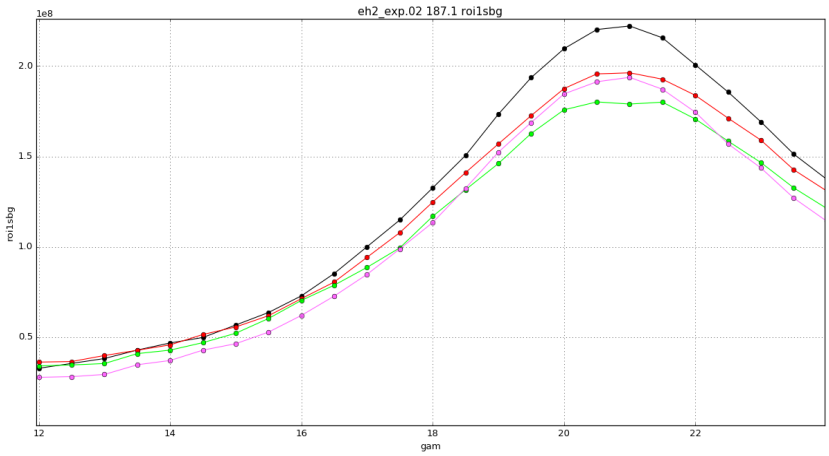

Figure 1(b): First diffraction peak (glass peak) of $15Rb_2O85SiO_2$. Black points are taken with a new sample, red points after 5500 s of measurement, green points after next 5500 s, pink curve after increasing the temperature from RT to 250°C. Sample position was kept constant.

References

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