Atomic dynamics in superionic conducting glasses

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In this experiment, we pursued two goals. The first was to show that aXPCS is a viable tool for studying atomic diffusion in glasses. The second goal was to gain insight into applying aXPCS to amorphous fast ionic conductors and to find promising ways to do detailed studies on these materials in the future.

The dynamics of single atoms is of fundamental interest in materials science. The processes on this scale govern both the fabrication and the stability of materials. Thus understanding the processes connected to atomic transport is of prime importance. Most of the experimental methods applied to measure diffusion are sensitive only for larger spatial scales on the order of a few tens of nanometers, which corresponds to thousands of atomic jumps. Atomic-scale X-ray Photon Correlation Spectroscopy (aXPCS) can reveal information about motion at the atomic scale. It is based on the connection of particular arrangements of atoms in a sample to their corresponding characteristic speckle pattern when scattering a coherent beam of X-rays. A change in the arrangement of atoms causes a change in the speckle pattern. Studying these changes as a function of time, one can obtain information on the atomic dynamics at various wavevector transfers. Combining the data of a range of scattering vectors allows to establish a model of the atomistic diffusion mechanisms in the material. This method is not limited by the elemental constitution and therefore makes a variety of systems accessible for investigation.

We successfully demonstrated the feasibility of studies of atomic diffusion by aXPCS in crystalline systems [1–4]. For amorphous media the absence of translational symmetry allows a much wider range of possible configurations. This makes developing a picture of the solid on the fundamental scale much more challenging. In amorphous solids, the atomic sites are arranged as a disordered network. Zachariasen [5] has identified certain structural motifs that act as the basic building blocks of network glasses at a local scale. Recent investigations obtained information about order also on longer scales [6]. On the other hand, the question of dynamics in amorphous media is far from solved. To gain insight into the dynamic processes in these systems, we studied the diffusion of the metallic glass $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$. We found that slow recrystallization processes slightly below the glass temperature have a large impact on the correlation times, thus it was impossible to measure dynamics in a glassy state in close-to-equilibrium conditions [7]. Consequently, we focused our attention on oxide glass forming materials like PbO-SiO_2.

The coherent set-up at the beamline P10 with 8 keV photons and a monochromaticity of $\Delta E/E \approx 10^{-4}$ was used, guaranteeing sufficient temporal coherence. Speckle patterns were recorded with a direct illumination CCD camera ($13 \times 13\,\mu m^2$ pixel size). The CCD camera was mounted about 60 cm downstream of the sample in order to have maximum scattered intensity while still resolving the speckles. The correlations in the resulting fluctuating speckle intensities were evaluated. For each wavevector $\vec{q}$, the measurement time was about 1 hour. In order to rule out spurious effects of sample thickness and homogeneity, we varied the scattering angle of the detector and kept the sample position fixed.

In the present beamtime, we did the first successful measurements on lead glass (see Fig. 1). With the high-intensity coherent beam, we have determined the form of the auto-correlation function at scattering angles below, in, and above the glass peak and the wavevector dependence of the correlation time.

With our experiments, we showed that measuring dynamics on the atomic scale in oxide glasses is feasible at temperatures of 643–713 K. We found that ion hopping takes place on well defined distances. With the new method of aXPCS, we directly observed the atomic network migration in

the binary glass former PbO-SiO_2 [8]. Thus the method of aXPCS is capable of resolving atomic dynamics on the atomic scale in glass forming materials.
As a second step, we looked into amorphous materials which have huge technical potential because of their ion conducting capabilities. Borate glasses are used in industry due to their superior properties for optical and electrochemical applications, e.g. as potential application as solid electrolytes in high energy density solid state batteries. They have the ability to incorporate a wide range of different elements, which makes them an ideal candidate to study the atomic motion mechanisms of ions through glasses. We experimented for the first time on alkali borate glass at temperatures of about 300 K. The additional complexity of borate glasses requires a different approach to achieve the goal of investigating their dynamics. Our first results indicate that the diffusion processes at this temperature in fast ionic conductors are way too fast to be resolved with current detectors with aXPCS. However, going to far lower temperatures helps overcome this problem, as will be shown in our next beam time report. The experiment will allow to measure the dynamics on the atomic scale in borate glasses and give insight into the ionic conductivity process on the atomic level. It will thus be possible to get a better understanding of the effects connected to ionic conductivity.

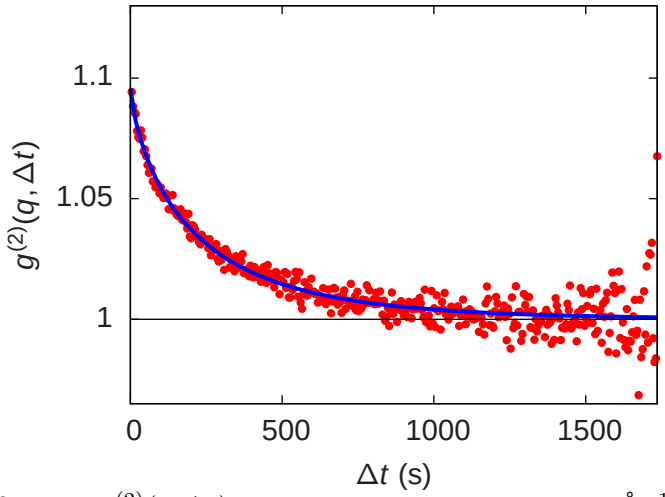

Fig. 1: Autocorrelation function $g^{(2)}(q, \Delta t)$ in $(PbO)_{60}(SiO_2)_{40}$ at $q \approx 0.85$ Å^{-1} and $T = 643$ K. Experimental values were fitted with $\alpha = 0.75$. The baseline is shown for comparison.

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