	Experiment title:	Experiment number:
ESRF	XPCS Analysis of Chalcogenide Glasses	HC-5099
Beamline: ID10	**Date of experiment**: from: 27/10/2022 to: 31/10/2022	**Date of report**: 27/02/2023
Shifts: 12	**Local contact(s)**: Yuriy Chushkin	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Jacopo Baglioni*[1]

Alessandro Martinelli*[1]

Peihao Sun*[1]

Francesco Dallari*[1]

Giulio Monaco*[1]

[1] University of Padova, Physics and Astronomy Department, 'Galileo Galilei', Italy

Report:

The experiment HC-5099 was proposed to elucidate the role of the structural changes on the dynamics induced by X-ray absorption as reported for the first time in [1]. In particular, we studied the binary glasses Ge-Se. The structural properties of the amorphous covalent network can be modified in a reproducible way changing the ratio between the two constituent elements. The selenium-rich glasses are characterised by a floppy network: the average number of bonds per atom is lower than its degrees of freedom (3 in a 3D structure). On the other hand, the network of Germanium-rich glasses is over-constrained, namely the number of constraints per atom exceeds its degrees of freedom. Unfortunately, chalcogenide glasses show clear permanent damages at doses far lower than the ones associated with borates and silicates under irradiation. Also, the induced decorrelation time turned out to be usually very short for the photon fluxes currently available at the ESRF (the decorrelation time is inversely proportional to the beam flux) and probably comparable with the maximum framerate of the EIGER4M. Finally, at a photon energy of 10keV the absorption length of our samples is of the order of 40um and the production of large disks with a comparable thickness via a standard polishing procedure is not trivial.

For these reasons, we opted to focus on two sets of samples: a group of thin small disks and a group of large disks whose thickness was a few millimetres. The former was employed for measurements in transmission geometry whereas the latter was used in a reflection configuration. Although the scattering in reflection is seldom exploited in traditional XPCS measurements, it has significant advantages when chalcogenide glasses are considered. Since the probed region is defined by the attenuation length, the thickness of the sample can be arbitrarily chosen. Also, the beam footprint on the sample is larger than the beam section causing a reduction of the decorrelation time due to its linear dependence on the inverse of the dose-rate [1].

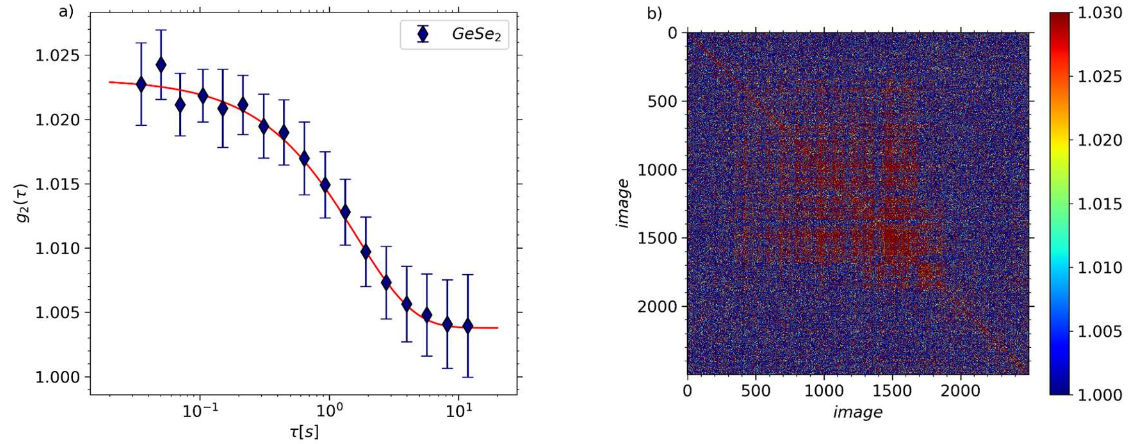

Figure 1: a) Intensity-intensity correlation function obtained in reflection geometry on Germanium diselenide. b) Two-times intensity correlation function obtained in transmission geometry on $GeSe_3$.

We studied five compositions of the family Ge_xSe_{1-x} (x=0.05,0.1,0.15,0.20,0.25). In order to improve the statistics, we repeated each measurement several times performing small meshes on the samples. The XPCS analysis of the glasses with the highest concentration of Germanium in reflection geometry was successful as reported in Fig1. a). The intensity-intensity correlation functions have a good contrast with a low level of noise. Also, the calculated decorrelation time is consistent with the dose rate associated to the beam footprint and the results obtained in transmission. Although the analysis is still ongoing, the same analysis on the selenium-rich glasses is troublesome. The estimated contrast is far lower than the value expected from simple geometrical considerations. Furthermore, the decorrelation time is quite hard to evaluate. We are analysing the data in order to find out the possible reasons for these differences among the samples.

In the second part of the experiment, we worked in the usual transmission geometry with samples of the order of the absorption length of the X-ray photons. We studied four different photon fluxes at room temperature to characterise the induced dynamics. Unluckily, a comprehensive comparison of the responses of the different glasses seems to be challenging due to an unexpected effect. In panel b) of Fig.1 an example of two-times intensity correlation functions is reported. The observed dynamics is clearly not stationary and shows sharp changes in contrast. These features in the two-times correlation functions are difficult to interpret: if the scattering volume changes during the measurements (e.g, vibrations of the X-ray beam or of sample holder) the effect on the dynamics is expected to be of this kind. For this reason, we are now working to understand if the observed dynamics is related to the sample or the experimental setup.

From a preliminary analysis of the data that we managed to analyse until now, it appears that the higher is the number of constraints in the amorphous network, the longer is the decorrelation time. Although a large part of measurements shows non-stationary dynamics (Fig.1b), we are working to maximise the amount of information derivable from the available data. However, the study of the combinations between network properties and dose-rates needed to quantitatively unveil the role of the network on the photon-matter interaction will likely require some additional measurements to be completed.

References:

[1] B. Ruta et al., Scientific Reports 7, 3962 (2017)