| | Experiment title: Two level states in ultra-stable and conventional glasses | Experiment number: HC-4933 |
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| **Beamline**: | **Date of experiment**: from: 26/04/2022 to: 02/05/2022 | **Date of report**: 12/09/2022 |
| **Shifts:** | **Local contact(s)**: Alexander Chumakov | *Received at ESRF:* |


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**Report:**

Aim of the experiment was to measure the density of vibrational states (DOS) at low frequencies of an ultrastable glass (USG) and to compare it with that of the corresponding conventional glass. The DOS measurements were carried out at beamline ID18 of ESRF on thin films of TPD (chemical formula: $C_{38}H_{32}N_2$) prepared both as an ultra-stable and as a conventional glass. We have been able to measure for the first time the DOS of an ultrastable glass with an exceptionally high energy resolution of 0.2 meV. This result was achieved exploiting the recently developed spectrograph for inelastic X-ray scattering with nuclear resonance analysis (NRAIXS) equipped with a high-resolution monochromator with four asymmetrically cut Si-crystals. Samples of both the ultrastable and conventional glass were prepared at the University of Barcelona in the form of thin films of approximately 50 μm thickness deposited on a gold substrate, chosen because of its high critical angle of total reflection.

Initially, we tried a configuration with four slits at the spectrograph output to simultaneously measure the signal from four identical samples. We have chosen this geometry to increase the signal to noise ratio of the measurement. To do this, it was necessary to tilt the samples, since the four beams exited horizontally the slits at different vertical coordinates. The grazing angle ($\theta = 0.153°$) was chosen to be greater than the critical angle for total reflection of TPD samples ($\theta = 0.085°$) and smaller than the critical angle of the gold substrate ($\theta = 0.3°$); in this way, the inelastic scattering from the substrate could have been considered negligible with respect to the one of the glass samples. During the experiment, the reflectivity of the samples as a function of the grazing angle has been measured and there were no evident signals coming from the substrate. However, we realized soon that we couldn't work in this configuration, because the samples were partially transparent in the direction of the beam leading to a significant crosstalk between adjacent samples.

For this reason, we carried out the rest of the experiment in transmission geometry on a single sample at a time. We measured first the ultra-stable glass and afterwards the corresponding conventional one. The inelastic scattered X-ray radiation was collected by an avalanche photodiode (APD) detector located 1 mm above the sample, reaching nearly $2\pi$ of solid angle, while the transmitted beam was collected by a similar detector in a forward position to measure the instrumental response. We have chosen to span the energy range between -5 meV and +10 meV with an energy step of 0.02 meV; for each point, the integration time was set to 2 seconds. We performed a total of 65 and 33 scans for the USG and the conventional samples, respectively, corresponding to more than three days of integration. During the experiment, the structure factor of the glasses was measured several times, to check that the samples did not undergo crystallization.

In addition, it was necessary to measure the spectrum in an extended range, [-20, 410] meV, to be able to properly normalize the DOS on an absolute scale. To do that, the very high-resolution monochromator was replaced with a monochromator reaching an energy resolution of 1.8 meV. The energy step was fixed to 0.5 meV and 22 scans were collected. Due to lack of time, the extended spectrum was probed only on the USG. The measurement of this extended spectrum with a reasonable signal to noise ratio required approximately one day.

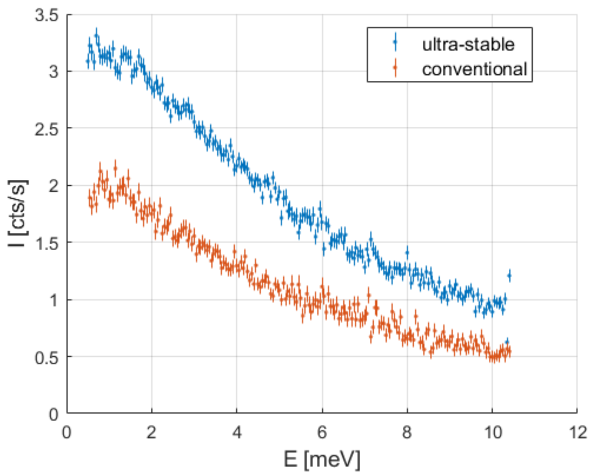


*Figure (1): energy spectra of ultra.stable and conventional glasses. The intensity is obtained by subtracting the elastic peak, by exploiting the instrumental response measured by the forward detector.*

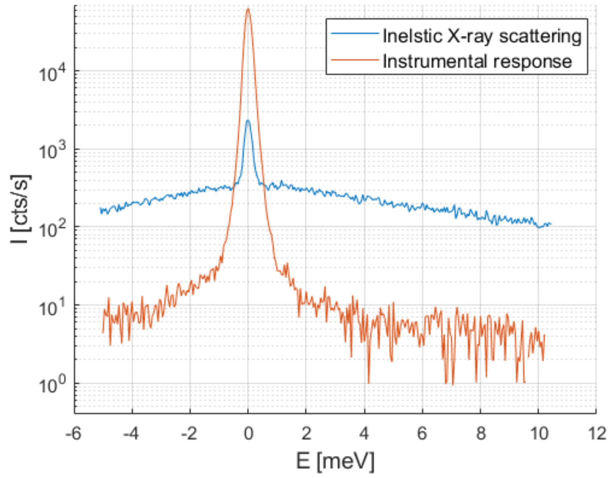


*Figure (2): the inelastic spectrum and the instrumental response fot the USG sample.*

The inelastic component of the high energy resolution spectra of the ultra-stable and conventional glasses are shown in figure (1). To obtain them, the scans are summed all together and the elastic peak is subtracted with care (figure (2)). From these results it is difficult to appreciate the differences between the ultra-stable and the conventional glasses, however we evaluated the DOS of both samples by using the extended spectrum measured on the ultra-stable glass. The results are promising, since the DOS of the conventional glass is larger than that of the ultra-stable one in the boson peak range, as expected. In addition, for both types of glasses, the specific heat obtained starting from the DOS seems in agreement with that measured via calorimetry experiments by colleagues in Madrid. It would be very important to measure the extended spectrum of the conventional sample, to compare the densities of states avoiding the assumption that the spectrum is the same at high energy, since this is not granted a-priori.

We have submitted a continuation proposal where we ask just for the time required for the measurement of the extended (low resolution) spectrum on the conventional glass. Since the equivalent measurement on the USG required one day of integration, we ask only for two days of beamtime, to set up the experiment and measure the same quantity on the conventional glass. This second measurement should definitively clarify the normalization of the DOS of the two glasses and allow a proper comparison with the specific heat data. Such a comparison is of great interest for the glass community and represents the first measurement of the DOS of an ultrastable glass with such a high energy resolution. For this reason, we expect to publish the result in a high impact journal.