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Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Resolving molecular arrangement in ultra-stable glasses by PDF calculation	**Experiment number**: MA-2273
Beamline: 11	**Date of experiment**: from: 26/11/2014 to: 30/11/2014	**Date of report**: 22/02/2015
Shifts: 12	**Local contact(s)**: Andrea Bernasconi	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Marta Gonzalez-Silveira*
Cristian Rodríguez-Tinoco*
Joan Ràfols-Ribé*
Javier Rodríguez-Viejo

Group of Nanomaterials and Microsystems, Physics Department, Sciences Faculty, Universitat Autònoma de Barcelona, 08193 – Bellaterra (Barcelona), Spain

Report:

In this experiment we measured the diffraction patterns in transmission geometry of organic glassy thin films up to high *q* in order to calculate the corresponding Pair Distribution Functions (PDF). The final goal was to determine differences in the molecular arrangement between glasses of different stabilities.

Introduction

The recent discovery of the so-called ultrastable glasses (UG) has opened new approaches to the understanding of the glass transition. These glasses are obtained by vapour deposition techniques (PVD) and their stability strongly depends on the deposition conditions. A conventional glass (CG), formed upon cooling of the liquid, would need millions of years of aging in order to achieve the same stability as ultrastable glasses. These glasses have lower enthalpies, higher relaxation times, lower densities and lower expansion coefficients compared to the conventional glass. The fact that their physical and chemical properties are between the conventional glass and the crystal has been pointed out by some researchers as an evidence of ultrastable glasses not being real glasses but nanocrystalline materials. Another characteristic feature of ultrastable glasses is an anisotropic extra low-q peak in a 2D WAXS measurements respect to the conventional glass caused by the anisotropic packing during the vapour deposition.

We intend to obtain information about the molecular arrangement of the ultrastable glass by calculating the PDF from glasses of different stabilities. The PDF allows the identification of different levels of order in an apparent glassy system which cannot be seen in a conventional X-ray diffractogram. Therefore, we expect the PDFs obtained to allow us to distinguish nanocrystalline systems from purely amorphous ones.

Experimental setup

Thin films between 5-10 μm of glassy Indomethacin and Celecoxib were deposited on 2x2mm^2 Si wafers by PVD in our lab. By modifying the deposition conditions we prepared samples of three different stabilities (ultrastable, medium and low). Two-dimensional diffraction images were taken with a CCD detector with 2048x2048 pixels. 40 keV were used in order to achieve 15 Å^{-1} in q, enough for a PDF calculation in organic glasses. In order to avoid reflections from the Si substrate we worked in transmission geometry. *Figure 1*

shows the schematics of the experimental setup. The samples were mounted in a stage with translational movement in x, y, z, and rotational around x and y axes (in addition to the six movements allowed by the diffractometer) that allowed us to align the sample in order to obtain the highest signal to noise ratio and the minimum contribution from the substrate. The alignment of ~5 μm thin films with a 5 μm tall took long times. Despite the small size of the beam, its gaussian profile hit part of the substrate and produced high intensity reflections. In order to minimize this effect, both for the data analysis and to avoid damaging the detector, we scanned the sample (moving translation and rotation of z, tz and rz) to find the positions with the lowest substrate reflections.

We detected beam damage to our sample after ~100s of exposition. The damage could be observed both visually (the beam track could be seen on the sample) and by monitoring the disappearance of the low-q extra peak of the UG glass. Thus, we were forced to change the sample position after short times of measuring in order to have fresh sample in the beam path. For each sample we measured 6 positions by rotating around the z axis plus 3 positions in the z axis for each rotation, summing a total of 28 fresh positions per sample. In each position about 50-100 frames in scans of 1-5s were taken to avoid saturation in the detector and to obtain a good signal-to-noise ratio, i.e. a total of 100s per position.

Measurements were carried out at 283K. The temperature of the samples was controlled with a N_2 cryostream. During the experiment we also moved the detector closer to the sample to gain q-range. For each position of the detector a capillary with ceria was measured as a calibration standard to get the geometrical parameters of our setup.

The particular geometry of our sample and setup caused us to invest about 1.5 shifts to prepare, align, find optimal positions and measure each sample.

Data reduction and results

The final 2D diffraction image for each sample and position was obtained as the average image of all the frames taken (see figure 2). The data reduction was carried out with the software package pyFAI along with the FabIO module for the reading and handling of 2D data (both written in Pyhton and supplied by the beamline).

First, the background image, mainly coming from the air scattering and the beam stop shadow, was subtracted from the averaged image. Afterwards, using the parameters provided by the processing of the ceria's calibration pattern, a 2D regrouping of the azimuthal integration was carried out with the radial dimension being the momentum transfer q in Å and a binning of 1º for the azimuthal dimension spanning over ~60º around the center (beam position coordinates).

We were not able to get rid completely of the substrate reflections, seen as evenly spaced spots in the diffraction image. Due to the multiplicative Q factor when calculating the PDF (in the kernel of the Fourier transform), the data noise and, in this case, the substrate reflections which are hardly visible in the diffraction pattern appear heavily amplified at higher q values. This leads to ripples in the PDF profile that could be mistakenly interpreted as real interatomic distances. It is important to emphasize that the the complex geometry of the experiment made it impossible to reproduce exactly the same reflections from the Si when measuring the bare substrate as a reference. In order to solve this issue, before reducing the 2D azimuthal profile to 1D, the values from the azimuthal dimension were sorted so that the higher values coming from the substrate reflection could be identified and removed. We were able to do this thanks to the amorphous and highly isotropic nature of our sample. In the case of the ultrastable glass, showing a low-q anisotropic peak, the azimuthal integration limits were taken close enough to the spot of the peak so that the resulting image could be also considered isotropic.

Once we had filtered and reduced each 2D image to a 1D spectra, the incident angle correction was applied using the parameters provided by the beamline staff.

The pair distribution functions were then calculated using the 1D spectra (intensity versus q) resulting from the above explained data treatment. The processing of the data was carried out using the software PDFgetX3. The results are shown in figure 3 for an ultrastable and a conventional glass of indomethacin. The three subplots show, respectively, the typical diffraction pattern in $Å^{-1}$, the reduced structure function f(q) also in $Å^{-1}$ and the resulting PDF in Å for both samples, ultrastable and conventional.

The peaks at 1.4Å and 2.4Å correspond respectively to the intermolecular C-C and C-C-C distances, which are present in all organic materials. The appearance of these peaks gives certain legitimacy to the calculated PDF.

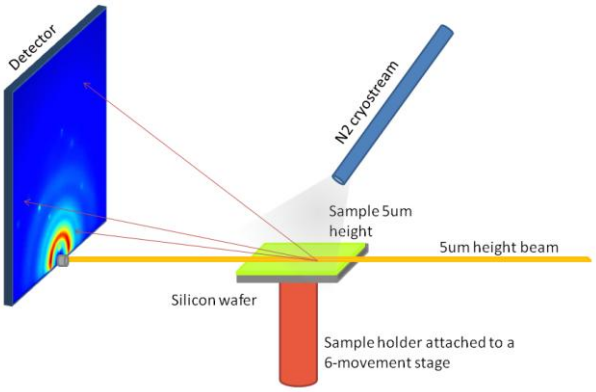

Figure 1. Experimental setup

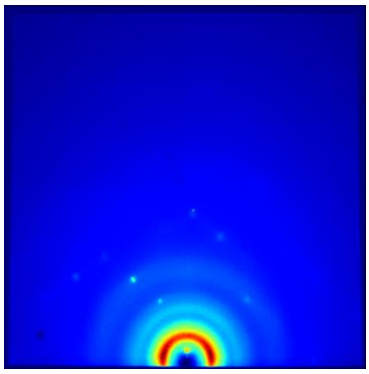

Figure 2. Averaged image of 100 diffraction frames of 2s each.

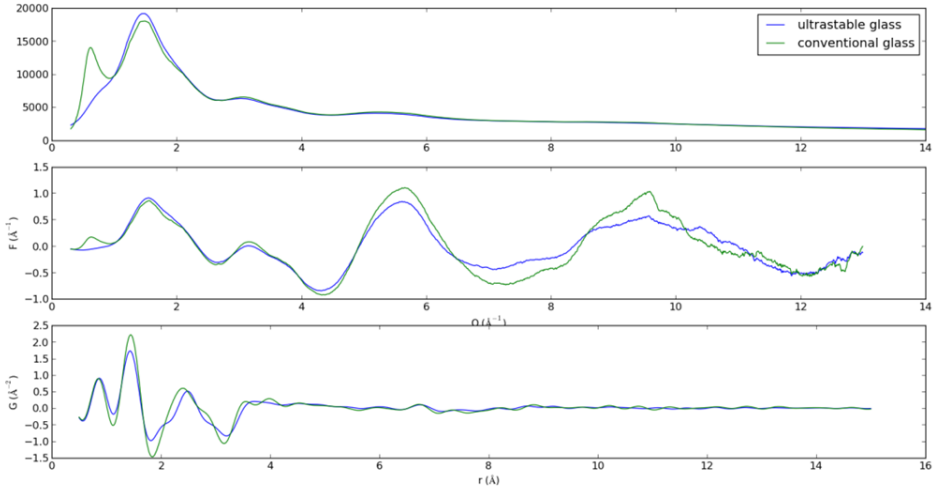

Figure 3. Top: 1D diffraction spectra from a conventional and an ultrastable glass, the horizontal axis being q in Å^{-1}. The diffraction profile of the ultrastable glass clearly shows the characteristic peak at low-q. Middle: reduced structure factor for each sample. Bottom:, calculated PDF for both samples. The short range of both PDFs is characteristic of an amorphous sample. The little differences seen between the samples can be attributed to the substrate reflections, which were different for each position and sample.

One of the goals of this experiment was to study the nanostructure of the ultrastable glass. When comparing the PDF obtained from the ultrastable and the low stable glasses, we see no significant differences. We can conclude, therefore, that the ultrastable glass is truly amorphous, considering that a nanocrystalline film would produce a different PDF, more similar to a damped crystalline profile.

Regarding the anisotropic packing of the ultrastable samples, we would expect a much more subtle effect on the PDF. Specifically, we would expect to see differences, if any, at intermolecular distances and slightly farther (around ~3Å and above). The little differences between the PDFs of the ultrastable and the conventional glass that can be observed in the bottom image of figure 3 are not significant, since they are within the uncertainty of the measurement. We did obtain differences of the same order between PDFs corresponding to the same sample. We attribute this uncertainty mainly to the non-complete subtraction of the silicon reflections.

As a final conclusion, we consider that given the technical capabilities of this beamline it would be very interesting to repeat some measurements with much thicker samples. Samples of ~50µm scanned with a beam of ~5 µm should allow us to avoid completely the substrate reflections and get more reliable PDF.

The work presented in this report will published in brief together with complementary experiments performed on similar samples.