



	Experiment title: Study of length-scale and temperature dependence of the structural relaxation in the fragile CKN glass-former	Experiment number: HC1735
Beamline: ID10	Date of experiment: from: 28/01/2015 to: 03/02/2015	Date of report: 06/03/2015
Shifts: 18	Local contact(s): Beatrice Ruta	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Giovanna Pintori*, Giulio Monaco* Università degli Studi di Trento, TN IT – 38050 Povo. Giacomo Baldi* National Research Council (CNR) Institute of Materials for Electronics and Magnetism (IMEM) Physics Department, Parma University, PR IT – 43124 Parma.		

Report:

The aim of the experiment was to investigate the temperature and wave-vector dependence of the structural relaxation process in the glass-former CKN across the glass transition temperature, T_g , with x-ray photon correlation spectroscopy (XPCS). Unfortunately, despite of numerous efforts, we were unable to perform these measurements because the sample – routinely used in our lab for optical spectroscopy experiments – underwent a beam-induced crystallization in a very short time. Figure 1 shows how the static structure factor $S(q)$ changes over time. Clear changes appear after a few minutes, and later on intense Debye-Scherrer rings appear in the scattering pattern, evidence of the fact that the sample was crystallizing. This is also very clear from the scattering patterns collected by the CCDs and shown in Figure 2. Unfortunately, despite all possible attempts (reduction of the incoming beam intensity using filters, different quenching procedures and temperature protocols, preparation of samples with different thickness) we could not avoid this beam-induced effect. We want to underline once more that the same sample does not show any signature of crystallization under the laser beam in our laboratory.

In order not to waste the beamtime, we used the last three days of beamtime to carry out the XPCS measurements originally proposed for CKN on a different glass-former, B_2O_3 , at a q -value corresponding to the maximum of the structure factor (thus at the microscopic scale). In fact, we are looking for dynamic signatures of the glass-transition, and thus for signatures that are qualitatively independent of the particular glass-former we are investigating. We measured the XPCS signal from B_2O_3 on cooling the sample from 260 °C where the sample is an ultraviscous liquid to room-temperature where it is in the glassy state.

We used samples with a thickness of about 130 μm to obtain a good compromise between optimizing the scattered intensity at the incident beam energy of 8.1 keV and matching the sample thickness to the longitudinal coherence length of the beam. The structure of the sample was regularly checked during the experiment by measuring its static structure factor. No sign of crystallization was detected in this case.

The XPCS data have been analyzed using a stretched exponential ansatz for the structural relaxation process [1]. The relaxation times obtained from this analysis are shown in Fig. 3 (red triangles), together with macroscopic data obtained with visible light scattering measurements carried out on the same sample in our laboratory in Trento (black symbols).

Our results indicate that: i) in the liquid phase the structural relaxation time measured with XPCS, τ_{XPCS} , is very close to that measured in the visible range; ii) in the glass phase τ_{XPCS} is almost temperature independent and remains in the 100 s range, thus much faster than that measured in the visible range, where the structural relaxation dynamics appears to be arrested. The result obtained in the liquid phase has to be expected, at least qualitatively, based on available simulations [2]. The result obtained in the glass, instead, is surprising and at odds with available models and macroscopic measurements. The time-scale of the dynamics measured by XPCS in the glass state seems to have a beam-induced origin [3], which explains why it is so fast. However,

there are no evidences of radiation-damage (meaning permanent damage): the beam intensity simply fixes the time-scale of the dynamics. Information on the q -dependence of the structural relaxation in the glass would be very relevant in order to make a step further in our understanding of the nature of this process.

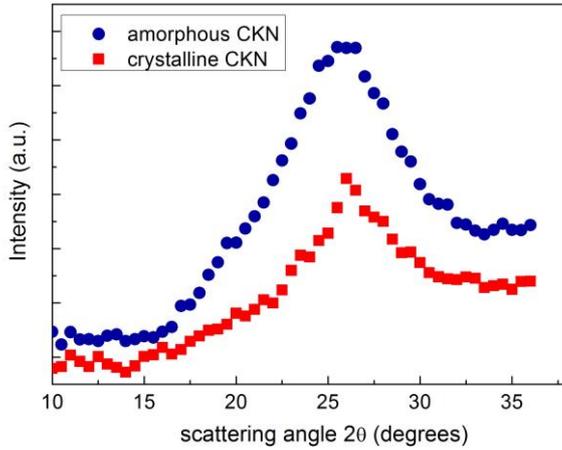


Figure 1: Static structure factor of CKN at different times during the crystallization of the sample.

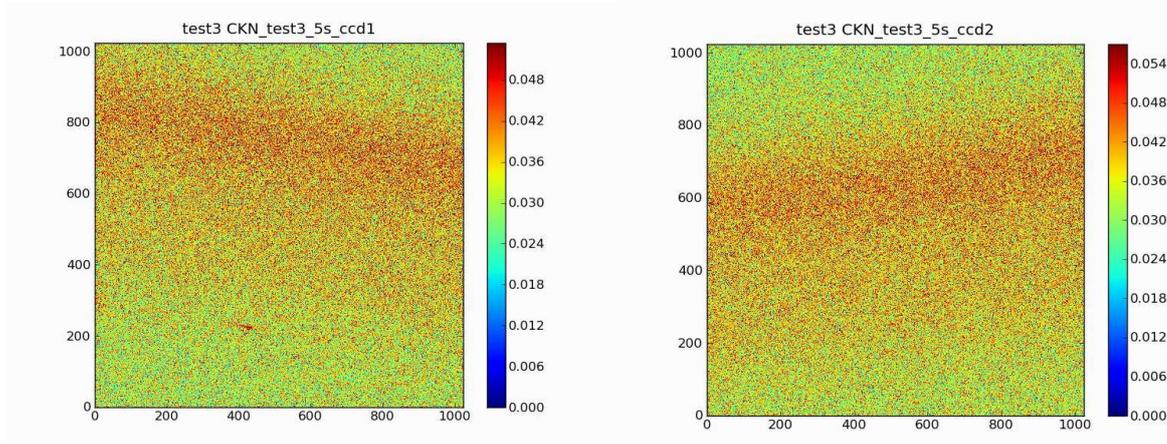


Figure 2: Speckles pattern of CKN during the crystallization process.

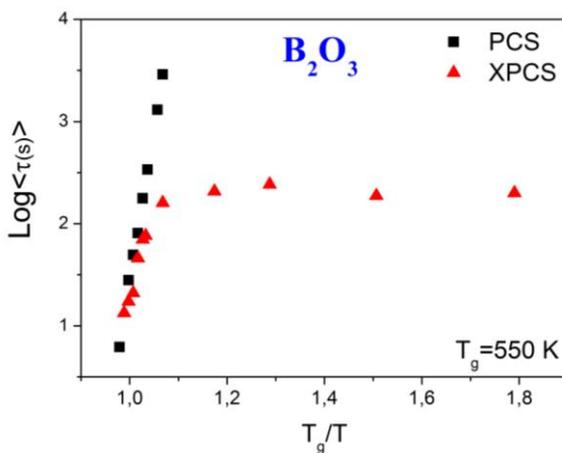


Figure 3: Arrhenius plot of the relaxation time measured using XPCS at $Q_{\text{max}}=1.5 \text{ \AA}^{-1}$ in B_2O_3 (red triangles). Black squares are macroscopic data obtained using visible photon correlation spectroscopy.

References

- [1] D. Sidebottom *et al.* Phys. Rev. Lett. **71**, 2260 (1993).
- [2] S. M. Bhattacharyya *et al.* J. Chem. Phys. **132**, 104503 (2010).
- [3] G. Pintori *et al.*, to be submitted.