ESRF	**Experiment title:** Vibrational Dynamics of nanocrystals: effects of the grain size reduction from the mesoscopic range towards the atomic scale.	**Experiment number**: HD-640
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Report:

The aim of the experiment was to measure the vibrational dynamics of nanocrystals with variable grain sizes in order to follow the evolution from a polycrystal to a glass. The most promising candidate was α-quartz, since we previoulsy studied in detail the dynamics of both the polycrystal and of the SiO_2 glass.

However the preparation of quartz nanocrystals appropriate for an IXS experiment has revealed to be very challenging. We managed to find a proper milling protocol to obtain a single grain size nanometric distribution with no amorphization, but for the purpose of the experiment the samples needed to be compacted to reduce the elastic signal coming form scattering at the grain-void boundaries. We managed to identify the proper parameters to compact the powder, avoiding any possible phase transformation from quartz to cristobalite, however we didn'y manage to obtain a sufficiently high densification to allow an IXS investigation of the samples. X-ray diffraction revealed not only the presence of small angle scattering, coming from the nanometric size of the powder, but also a diffused scattering background at all angles, coming from the disorder introduced in the quartz by the milling (dandling bonds, defects, vacancies..).

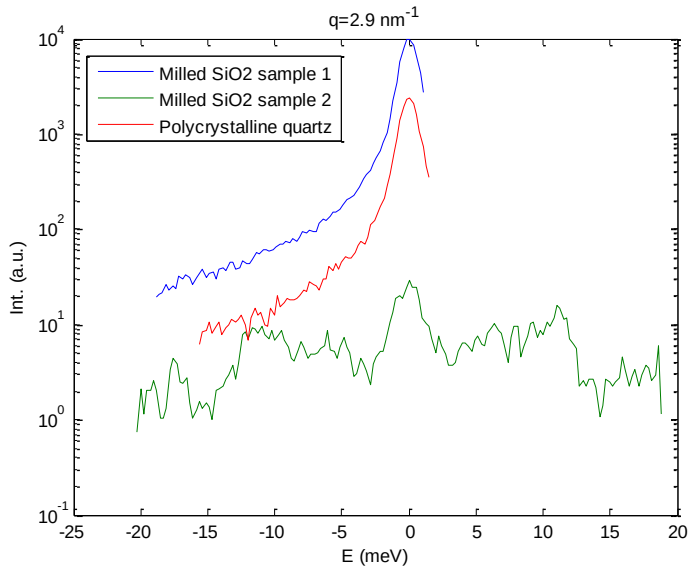

Figure 1: IXS spectra collected at an exchanged wave-vector q=2.9 nm^{-1} on two compacted pellets with nanometer sized grains and polycrystalline quartz with micrometer size grains.

This diffused scattering turned out to be a big problem when measuring at the ID28 beamline. Indeed the elastic scattering was so intense at all angles that it was impossible to detect any phonon signal (Figure 1). Since the elastic signal of the quartz nanocrystals was masking completely the inelastic features, we have changed of sample and we have measured ZrO_2, a sample that we were preparing at the same time as an alternative to SiO_2.

Yttria-stabilized cubic Zirconia

ZrO_2 can be stabilized in its cubic structure if doped with Yttria (Y_2O_3). As such, this is a quite disordered structure, because of the presence of oxygen vacancies.

This system has been chosen as alternative to SiO_2 for several reasons: 1) like SiO_2, it is an insulator, which means that every change in the thermal conductivity because of the grain size can be directly related to a change in the phonon dynamics, 2) it is quite isotropic, which reduces the effect of phonon broadening in the polycrystal due to the acoustic branches separation, 3) it can be grown as nanometer sized particles, so that no milling is needed, which would cause the same problems met with SiO_2.

We prepared 5 samples :

1) Densification 87% grain size 40 nm
2) Densification 94% grain size 30 nm
3) Densification 96% grain size 50 nm
4) Densification 96% grain size 90 nm
5) Densification 96% grain size 140 nm

The samples were then polished down to thicknesses of 100 μm and 50 μm, optimized for measurements at 17 and 24 keV respectively, corresponding to the energy resolutions of 3 meV and 1.4 meV of the IXS beamline. During the IXS experiment we had the time to investigate only two samples: we took the largest grain size (Sample 5) and the 40 nm grain size (Sample 1), the one with 30 nm grains having a larger small angle scattering, but an inelastic signal quite identical to the 40 nm. The very low signal didn't allow us to work at 24 keV (higher energy resolution), so the measurements were performed at 17 keV. We also measured the longitudinal modes of a single crystal of the same sample, in order to compare with the pellets. The spectra of the polycrystal are well described by a modelling function which includes the longitudinal acoustic phonon, a low-energy mode and a quasi-elastic Lorentzian signal, this latter probably due to the oxygen vacancy disorder in the crystal.

While the physical origin of the low energy mode and the quasi-elastic signal is still under investigation, these data give us the acoustic dispersion as well as the width of the phonons in the single crystal at room temperature, which we can compare with the data on the pellets. We find that phonons are quite broad, due to the intrinsic disorder of this system, and very rapidly disappear.

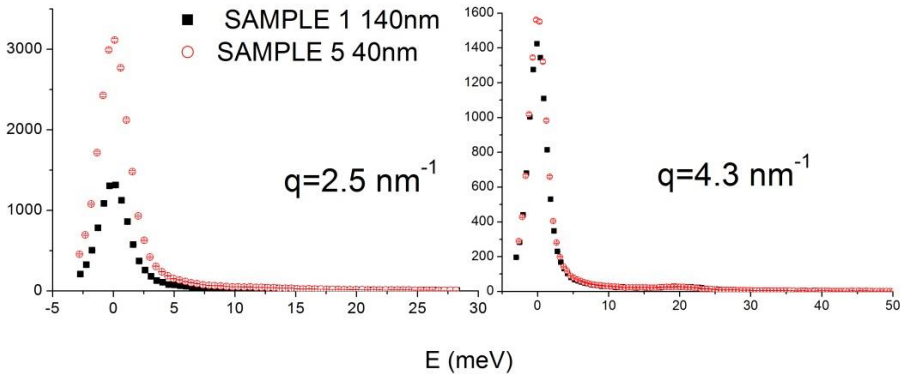

Figure 2: IXS spectra of the two pellets compared at two different q values.

Figure 2 reports two spectra collected on the two pellets at q=2.5 and q=4.3 nm^{-1}. It is clear that a huge elastic signal is present, coming from the small angle scattering caused by the nanometric size of the powder. Indeed the 40 nm size sample has an elastic line at low q which is twice the one of the 140 nm size sample. It is however possible to discern the phonons. From a fitting procedure we determined the dispersion curves and the broadening of the peaks. The detailed analysis of the spectra, with the comparison with the single crystal branches and with data for the thermal conductivity is ongoing.