ESRF	**Experiment title:** Transient disordered states on the route to $NaYF_4$:Eu luminescent nanocrystals	**Experiment number**: SC-4259
Beamline: ID02	**Date of experiment**: from: 15/04/2016 to: 18/04/2016	**Date of report**:
Shifts: 9	**Local contact(s)**: Dr. Sylvain Prevost	*Received at ESRF:*

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Objective and summary of results:

The aim of the session was to investigate the formation of luminescent $NaYF_4$:Eu nanoparticles in solution upon mixing of two cationic and anionic aqueous precursors ($Y_{0.95}Eu(NO_3)_3$ and NaF, respectively). The goal is to identify whether crystallization in an ionic solutions, where no speciation effects are expected, form via intermediate states ("non-classical" nucleation: liquid-liquid phase separation, amorphous particles, etc.) or by ion-by-ion growth (classical nucleation), and compare the structural data with theoretical predictions: time-evolution of the crystal/amorphous particles numeric concentrations, sizes, and volume fractions.

We aimed at collecting SAXS and WAXS data, in situ, in the 60µs to hour reaction time range. In order to span the complete reaction time range, we proposed to use three setups, namely i) a microfluidic setup (t=60µs – 10ms) ii) a stopped-flow setup (t=6ms – 10mins) and iii) a peristaltic setup (t =20s – 1h).

As a summary, we managed to collect SAXS and WAXS data in the 6ms-90mins reaction time range both for the $NaYF_4$:Eu synthesis, but also for a YF_3:Eu synthesis. A first analysis reveals clearly a non-classical nucleation scenario, and we expect from the data a complete study of the amorphous-to-crystal conversion. We were not able to carry out the reactions in the microfluidic chips; however, we could successfully record the SAXS/WAXS signal of ripened luminescent nanocrystals (YVO_4:Eu), which opens solid perspectives for another session to come.

Results:

$NaYF_4$:Eu and YF_3:Eu syntheses in the 6ms – 10mins reaction time range (stopped-flow setup).

Both reactions have been studied using our commercial stopped-flow setup. Prior to experiments, we have measured in the laboratory a minimal mixing time of 6ms using a chemical reaction with known kinetic constant.

We used acquisition times of 5ms (YF_3:Eu syntheses) and 20ms ($NaYF_4$:Eu). In order to record reaction times of 6ms without degradation of the temporal resolution by the acquisition time, we used a specific injection sequence allowing us to record 3 to 5 frames as the reactive mixture was flowing (hence, at a constant reaction time of 6ms), before stopping the flow. With this strategy, we recorded scattering patterns at reaction times of 6ms with an excellent signal-to-noise ratio (Figure 1). We observed that at such short reaction times, the low-angle scattering amplitude is already orders of magnitude higher than that of the precursors, while no Bragg peak is observed. This demonstrates that the nanocrystals form from a fractal amorphous matrix.

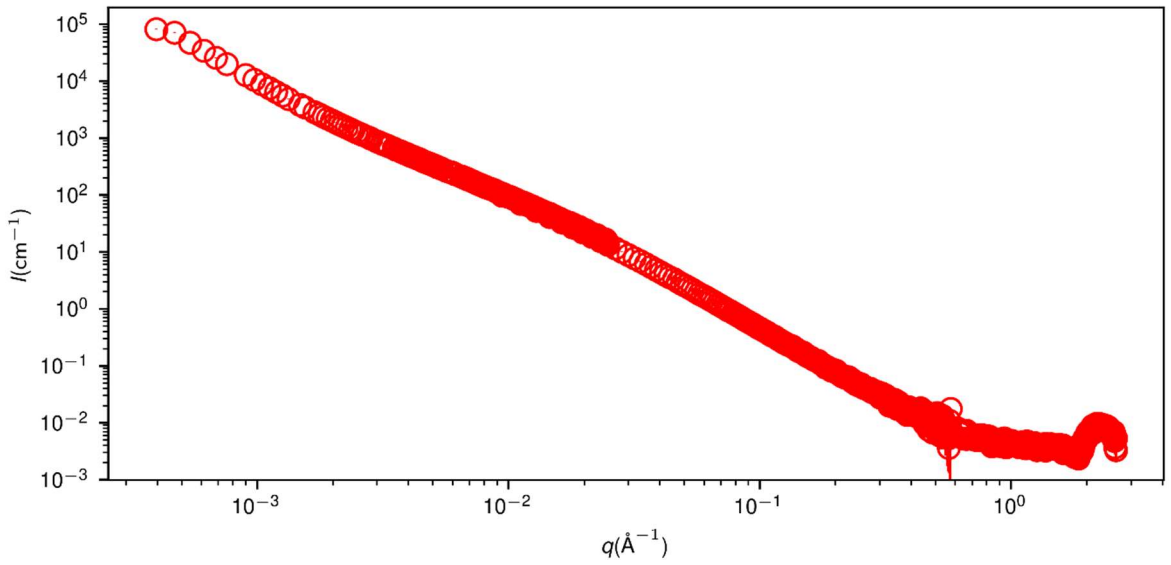

Figure 1. SAXS/WAXS pattern recorded for a $NaYF_4$:Eu reaction, at reaction time t=6ms, using the stopped-flow setup in a lost-flow configuration.

The SAXS/WAXS patterns at reaction times below t = 600s show some evolutions on either sides of q=0.01$Å^{-1}$, Figure 2, but no Bragg peak is observable (Figure 3). This is qualitatively assigned to the formation of nanometer-scaled particles with a crystal coherence length below 1nm, viz. amorphous particles, or small crystals. While the same trend is observed, with slower rate, for the YF_3:Eu synthesis.

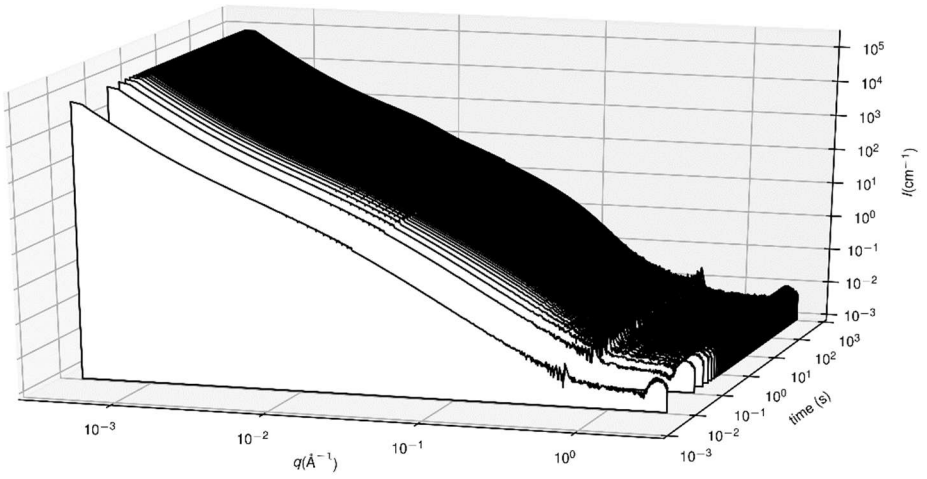

Figure 2. SAXS/WAXS patterns recorded during a NaYF4:Eu synthesis with the stopped-flow setup.

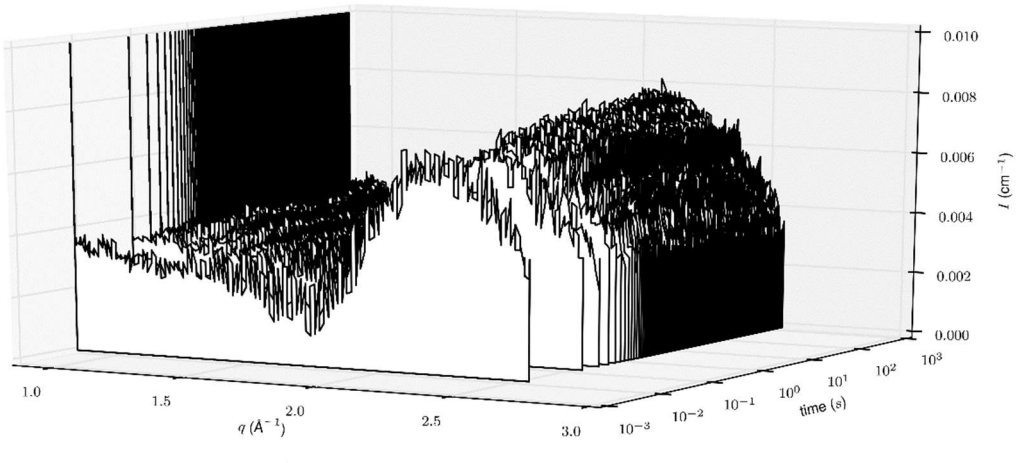

Figure 3. WAXS patterns recorded during a $NaYF_4$:Eu synthesis with the stopped-flow setup.

$NaYF_4$:Eu and YF_3:Eu syntheses in the20s–30min/1h reaction time range (peristaltic setup).

Longer reaction times could be recorded by carrying out the same $NaYF_4$:Eu and YF_3:Eu syntheses in a home-made setup where the reactive medium circulates in a closed loop using a peristaltic setup, and flows through the kapton capillary. We used acquisition times of 10 ms and 200 ms for USAXS and SAXS/WAXS, respectively.

During measurements, we have observed that the thickness of the kapton capillary changed significantly. This was due to a progressive collapse stemming from negative pressures induced by the circulation of the solution. However, we could correct offline for the thickness variation using the water signal as a reference. The post-treatment was validated by the consistency of the SAXS/WAXS data recorded with the stopped-flow setup; another indication of the validity is that the total volume

fraction of amorphous+crystal phase, calculated by the invariant theorem (integration of Iq^2) is found constant along the reaction, consistent with an amorphous-to-crystal conversion at constant volume fraction.

For both reactions, the early stages are consistent with the data recorded with the stopped-flow setup. At later stage, for $NaYF_4$:Eu, we observe a low-angle signature assigned to the formation of the nanocrystals simultaneously to the emergence of Bragg peaks (Figure 4 and Figure 5).

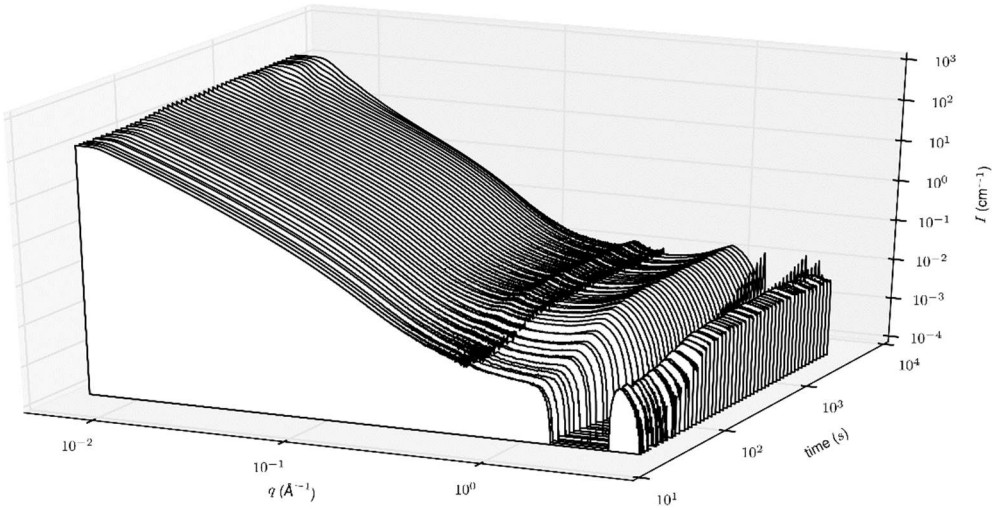

Figure 4. Selected SAXS/WAXS patterns recorded during a $NaYF_4$:Eu synthesis with the peristaltic setup.

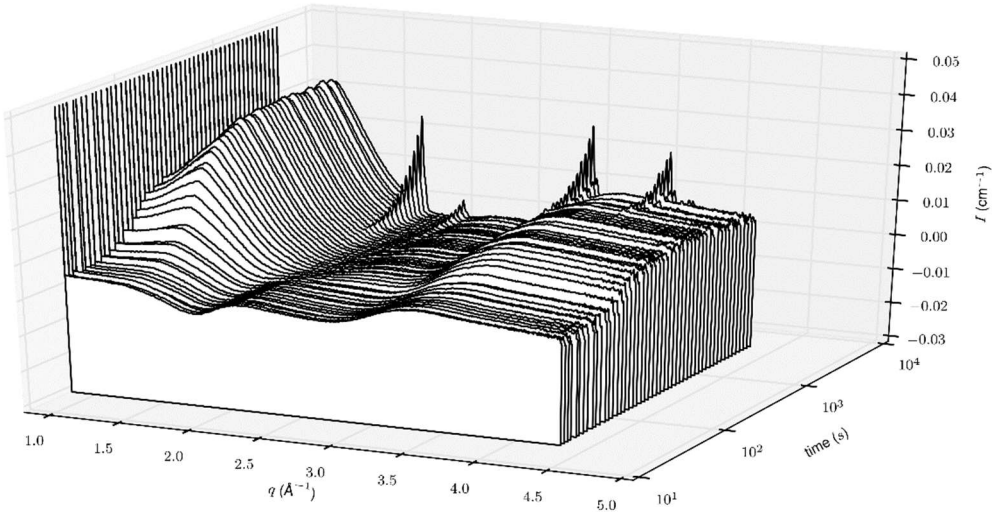

Figure 5. Selected WAXS patterns recorded during a $NaYF_4$:Eu synthesis with the peristaltic setup.

While for YF_3:Eu, there is a significant change of signal detected below q<0.1 Å^{-1} (Figure 6) but with no evidence of crystallization in the wide angle between 1-4.5 Å^{-1} (Figure 7). This clearly indicating that amorphous network – amorphous particles – crystal transformation is occurring in the YF_3:Eu synthesis.

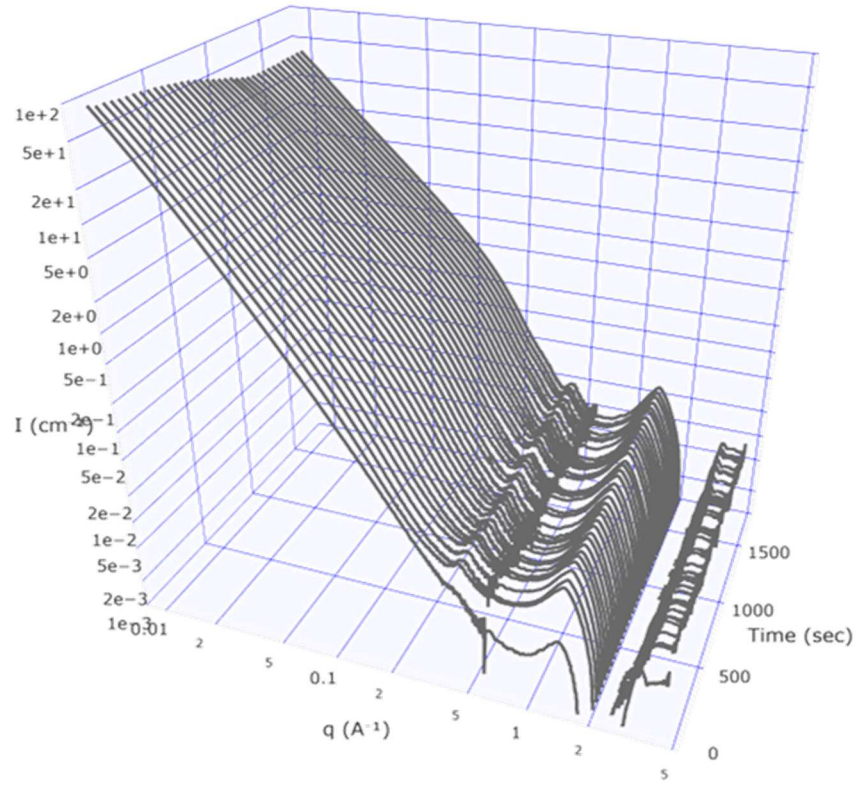

Figure 6. Selected SAXS/WAXS patterns recorded during a YF_3:Eu synthesis with the peristaltic setup.

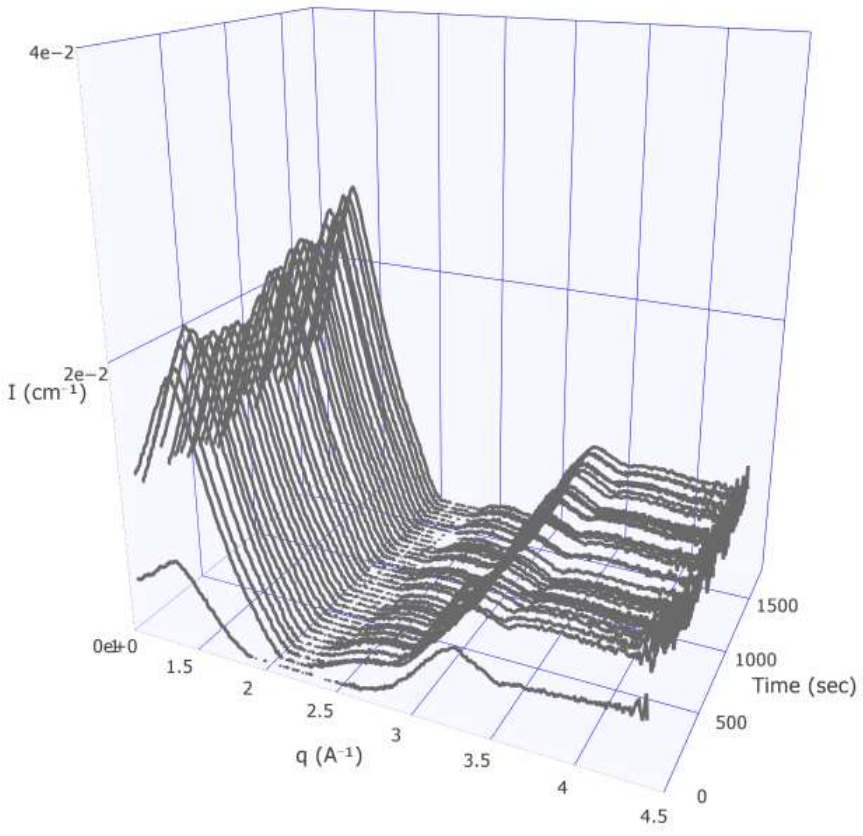

Figure 7. Selected WAXS patterns recorded during a YF_3:Eu synthesis with the peristaltic setup.

YVO_4:Eu nanoparticles in the microfluidic chips.

The microfluidic chips have been designed and constructed in our laboratory. They consisted of a mixing unit (a so-called "butterfly mixer") followed by an inspection channel which was 50µm thick in the direction of the beam, and 100µm wide perpendicular to the beam. The chip was constructed in a UV-curable optical glue. Prior to experiments, we had checked that the chips are X-ray transparent and poorly scatter. The chip were mounted on the beamline with a home-made stage.

We needed one full shift to align the chip with water flowing, by measuring the X-ray transmission. We finally succeeded in recording the SAXS/WAXS signal of YVO_4:Eu nanoparticles (40nm diameter) flowing in the observation channel. After subtracting the signal from the chip with water flowing and dividing by the nominal thickness of the channel (50µm), we recovered a SAXS/WAXS signal which is in very good agreement with that of the same sample measured in a 2mm-thick kapton capillary (Figure 6 and Figure 7).At 1.2$Å^{-1}$, we also observe a broad peak which increases as the chip is scanned, assigned to beam damage. However, it doesn't overlap with the regions of interest.

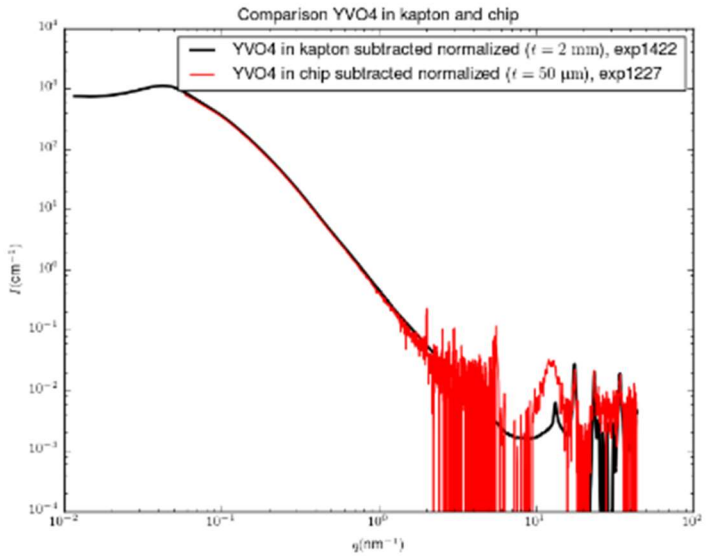

Figure 6. SAXS/WAXS signal of a dispersion of YVO4:Eu nanoparticles in water measured in a 2mm thick kapton capillary (black, 5ms acquisition time), and in a 50µm thick microfluidic channel (red, 10s acquisition time).

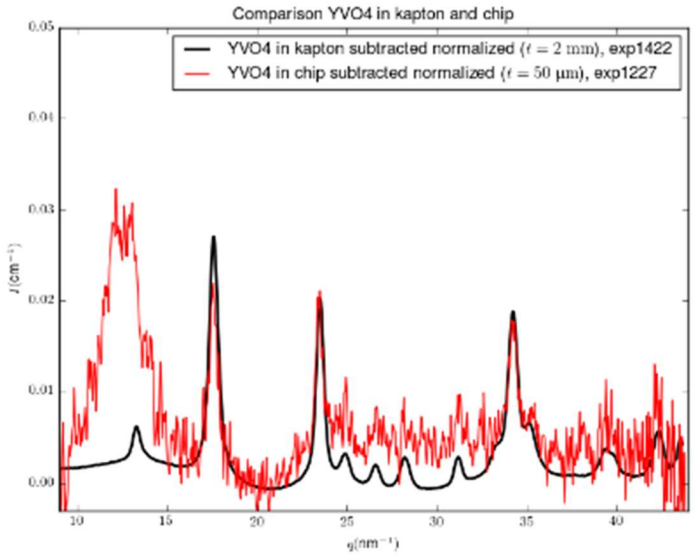

Figure 7. SAXS/WAXS signal of a dispersion of YVO4:Eu nanoparticles in water measured in a 2mm thickkapton capillary (black, 5ms acquisition time), and in a 50µm thick microfluidic channel (red, 10s acquisition time).

This microfluidic session allowed us to conclude that the chip are suitable for use in SAXS/WAXS experiments. We decided the following improvements after the session: i) increase the channel thickness along the beam to 80µm ii) design a portable optical setup to be carried to the beamline for the experiments to come, and iii) mount the chips under a laminar hood, either portable or available at ESRF.

Justification and comments about the use of beam time:

9 shifts were allotted. They have been utilized as follows: 1 shift was used for aligning the microfluidic chip and recording water and YVO_4 nanoparticles using it. After microfluidic testing, another shift was utilized to configure the beam and detector for the continuous flow set-up. 3 shifts were dedicated for following syntheses ($NaYF_4$:Eu and YF_3:Eu), between 20s–30min/1h reaction times, using peristaltic set-up. 2 shifts were devoted for final states measurements and for modifying the configuration suitable for stopped flow experiments. 3 shifts were used for following syntheses ($NaYF_4$:Eu and YF_3:Eu), between 6ms-10 min reaction times, using stopped flow.