ESRF	**Experiment title:** Transient disordered states on the route to $NaYF_4$:Eu luminescent nanocrystals	**Experiment number**: SC-4367
Beamline: ID02	**Date of experiment**: from: 27/01/2017 to: 30/01/2017	**Date of report**: 24/03/2018
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 YVO_4:Eu nanoparticles in solution upon mixing of two cationic and anionic aqueous precursors ($Y_{0.95}Eu_{0.05}(NO_3)_3$ and Na_3VO_4, respectively). From previous experiments, we knew that the formation of these nanoparticles occurs via an intermediate amorphous network, i.e. belongs to the family of non-classical nucleation processes. We have shown that the amorphous network already shows two characteristic sizes that determine the two characteristic sizes of the final nanocrystals, namely i) the size of the nanoparticles (40nm), and ii) the size of the primary grains (2nm-40nm, depending on the pH) which constitute them. Here, we wanted to follow the formation of the amorphous network itself, and in particular the emergence of both sizes from the ionic solutions.

We aimed at collecting SAXS and WAXS data, in situ, in the 60µs to minute reaction time range. In order to span the complete reaction time range, we proposed to use two setups, namely i) a microfluidic setup (t=60µs – 10ms) ii) a stopped-flow setup (t=6ms – 10min).

In summary, we managed to collect SAXS and WAXS data in the 6ms – 10min reaction time range for syntheses of YVO_4:Eu with two different pH values (one with small primary grains, named V2; one with large primary grains, names V3), and for variable precursor concentrations. A first analysis reveals we could capture the late stage of formation of the amorphous network that terminates at 100ms for the slowest (most dilute) synthesis. The observations are compatible with a diffusion-limited aggregation of nanometer-sized clusters However, the conclusions remain unambiguous as the data were collected above a reaction time of 6ms, that is, much larger than the characteristic time of formation of the amorphous network, estimated to e.g. 70µs for the most dilute synthesis. We were not able to carry out the reactions in the microfluidic chips due to chip breakdown after 8 hours of use (alignment of the chip and recording of references). This outlines the need to improve chip reliability offline for extended periods of time (typically 8 hours) before submitting any new proposal.

Results:

YVO_4:Eu syntheses in the 6ms – 10mins reaction time range (stopped-flow setup).

Syntheses with two different pH of precursor solutions, each at three different concentrations, 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 20ms (YF_3:Eu syntheses) to SAXS/WAXS patterns. 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).

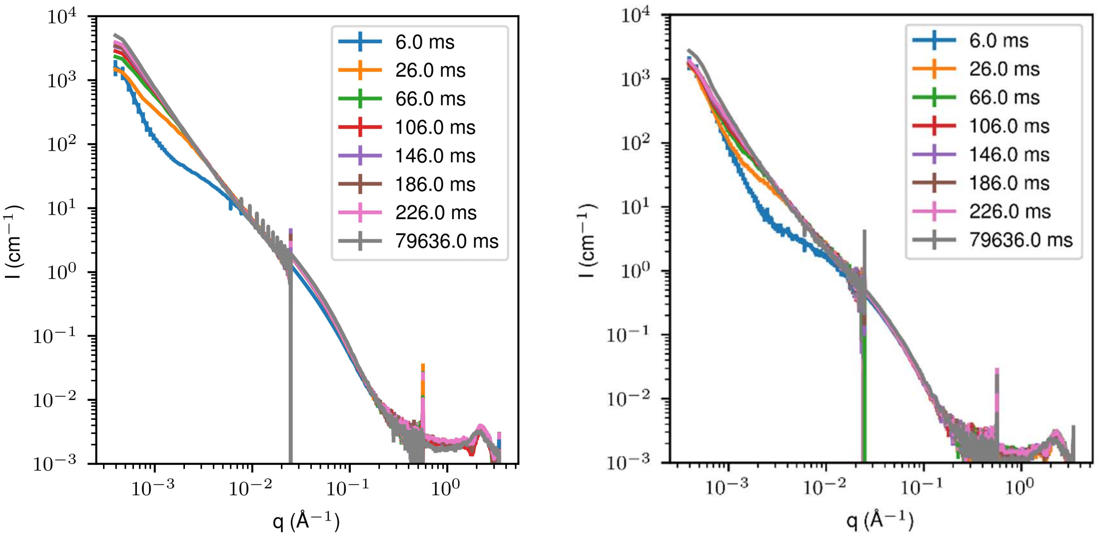

Figure 1. SAXS/WAXS pattern recorded for YVO_4:Eu reactions, for a high-pH synthesis. Left: precursor concentration of 5mM, and right: 1.7mM.

After a reaction time of 1min, we observe the typical scattering pattern already observed previously, characteristic of the fractal amorphous network from which the nanocrystals later nucleate. In particular, we observe a power-law decay at low angles, followed by a correlation signal characteristic of nanometer-sized amorphous particles. In the 6ms – 100ms range, we observe systematically an increase in the low-q signal, whereas the large-q signal varies only marginally. It is tentatively assigned to the growth of the amorphous network by polymerization of already existing amorphous particles. The increasing total scattering signal, related to an increase in total volume fraction, is an indication that the polymerization occurs via formation of new solid-state products. The characteristic reaction time, estimated by an exponential law, varies in the τ = 5µs – 70µs range, and decreases consistently as the concentration increases.

In the treatment to come, we will extract the evolution of the total volume fraction of the fractal network, of the volume fraction of the constituting amorphous particles, and the size and number of particles. Although the data discussed here will be insightful, we already now they will be restricted to reaction times well above the characteristic reaction time ($t > 10 – 20x\tau$).

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 80µm wide perpendicular to the beam. The chips were constructed in a UV-curable optical glue. Prior to experiments, we had checked that the chips are X-ray transparent and poorly scatter. The chips were mounted on the beamline with a home-made stage, and a retractable home-made optical setup was used for alignment.

Before starting the session, we had identified one chip (Figure 2) that could stand a flow rate of 2 µL/s in two channels. This chip could be mounted at ESRF and we could flow water during about 8 hours. The location of the outlet channel (filled with water) was precisely identified, based on the scattering signal induced by the channel edge. More precisely, we have used the scattered signal (integrated both "radially" and over small *q*) to identify the channel edges as this signal increases when crossing a border. Unfortunately, just before switching to precursor solutions, the chip stopped working (fluid did not flow out anymore) and a leak appeared. Several chips were unsuccessfully tested in the next day.

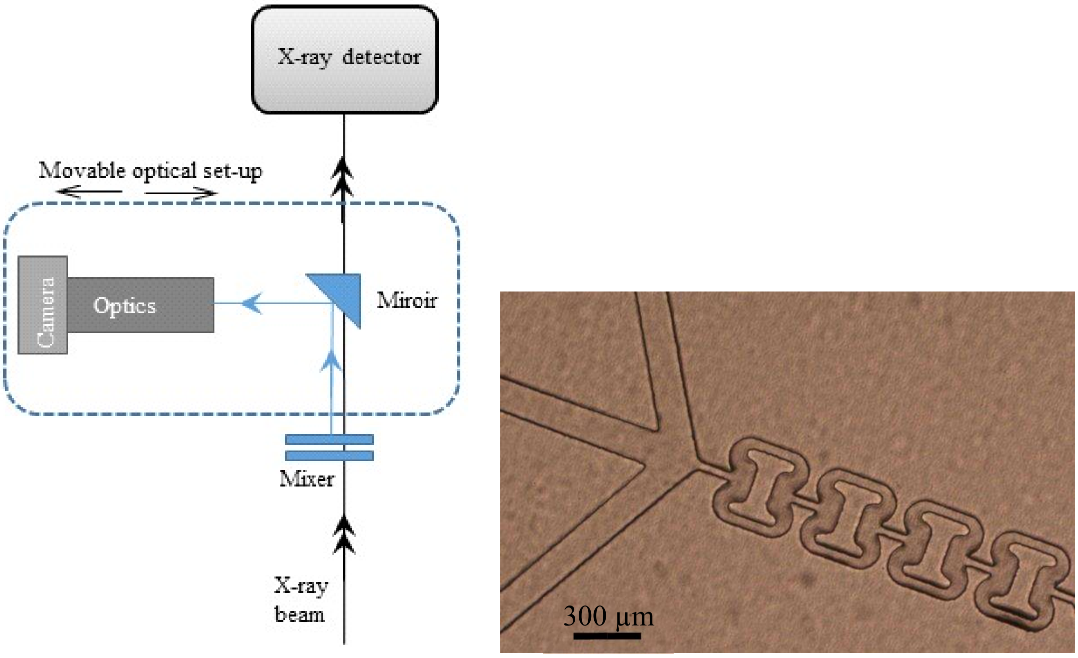

Figure 2. Left, scheme of the optical setup mounted on the beamline; right, image of the chip used at ESRF.

As perspectives for improvement, we will i) redesign the housing of the chip and improve chip bonding in order to prevent leaks more efficiently, ii) improve the thickness homogeneity of the chip by additional patterning of the mold, in order to improve the tubing-to-chip tightness, iii) improve the chip production efficiency, by selecting materials which are more easily processable, and iv) allow the chip housing to accommodate a capillary (2mm in diameter) for measuring standards (Si powder for WAXS and sodium behenate for SAXS. These improvements have been since addressed in our laboratory.

Justification and comments about the use of beam time:

9 shifts were allocated. They have been utilized as follows: 1 shift was used for aligning the first microfluidic chip and recording water signal. 2 additional shifts were used to try other chips. 3 shifts were dedicated for following three YVO4:Eu syntheses at low pH and different concentrations between 6ms – 10 min reaction times, using the stopped flow setup. 3 shifts were used for three YVO_4:Eu syntheses at high pH and different concentrations.