ESRF	**Experiment title:** Near-Field Ptychographic Tomography of Liquid-to-Crystal Transformation in Cerium Oxalate Precipitation	**Experiment number**: HC 5283
Beamline: ID16a	**Date of experiment**: from: 25 Feb 2023 to: 28 Feb 2023	**Date of report**: 1/9/2023
Shifts: 9	**Local contact(s)**: Dmitry Karpov	*Received at ESRF:*

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Report:

The goal of this experiment at ID16A was to investigate the suitability of holotomography (HT) and near-field ptychographic tomography (3DNFP) for performing measurements of freeze-quenched reactive solutions undergoing liquid-liquid phase separation (LLPS) and subsequent crystallization. Previous experiments at the cSAXS beamline of the Swiss Light Source (SLS) confirmed these measurements were possible with far-field ptychography, but these required the use of small ~10 µm pulled capillaries that excluded forming crystals (of several 10's of µm). We sought to take advantage of the full-field 3DNFP capabilities of ID16a to analyze larger capillaries (~50-80 µm ID) that would enable us to observe both phase-separated liquids and crystals concomitantly.

Over many years, we have studied the crystallization of cerium oxalate (CeOx) and demonstrated using several techniques including *in situ* small-angle X-ray scattering (SAXS) and cryogenic transmission election microscopy (cryoTEM) that transient liquid and amorphous phases form as precursors to the final thermodynamically stable crystalline phase.[1] For all experiments, including these at ID16a, the precipitation reaction is initiated by combining aqueous solutions of cerium nitrate hexahydrate and oxalic acid using a fast millifluidic mixer that mixes the two reactants in ~250 ms.[2] In the case of 3DNFP measurements, aliquots from the outlet of the mixer were transferred into a glass capillary using a micropipette and plunged in liquid ethane. To account for the low thermal conductivity of the thick glass walls and the slow freezing rate of a such a large sample, we added 30 wt% glycerol to our reactive solutions as a cryoprotectant. However, initial 3DNFP measurements revealed the formation of large ice crystals and also significant radiation damage during long exposures resulting from the organic additive (**Fig. 1**). Therefore, to at least be able to perform long high-resolution scans without radiation damage, we prepared new samples without glycerol.

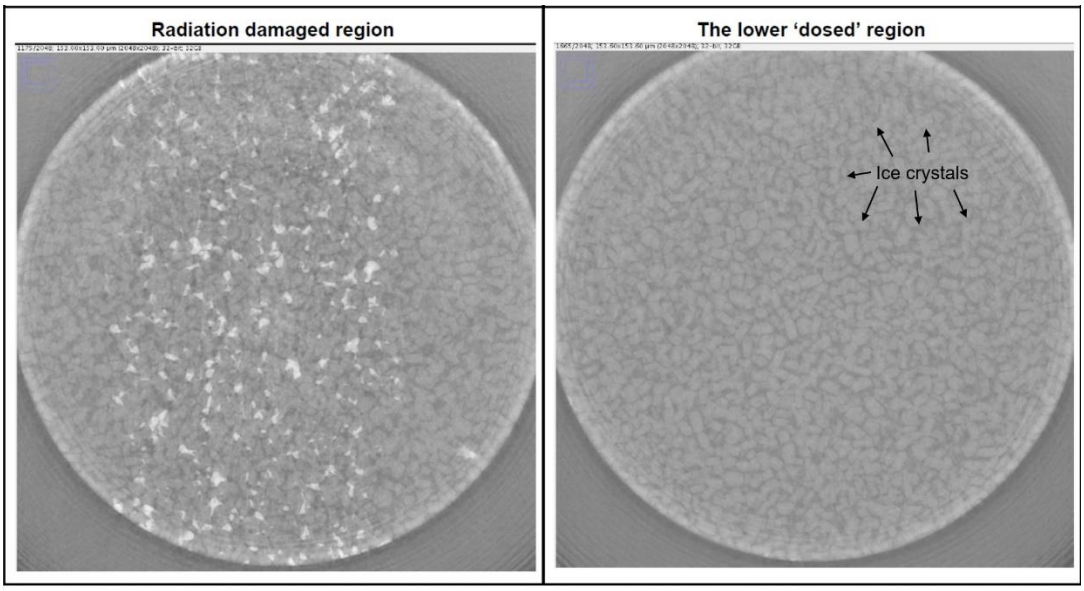

Figure 1: Holotomograms of frozen samples with 30 wt% glycerol showing ice contamination and radiation damage.

Surprisingly, these samples had fewer noticeable ice crystals than with the cryoprotectant (**Fig. 2a-d**). In both 3DNFP and HT measurements, apparent liquid phases and amorphous solid particles with different electron densities could be observed, similar to our previous experiments at the SLS. Not surprisingly, the 3DNFP measurements produced higher quality data, justifying the longer scan times required for future experiments on similar samples. However, some signs of ice formation were still noticeable, and it was observed that "liquid" phases would aggregate at the grain boundaries between hexagonal ice crystals (**Fig. 2e**). These observations introduce uncertainty into our experiments, and together with recent control experiments performed at the SLS, suggest that the observed "liquid" phase is a combination of our target phase of interest and ion condensates excluded from the ice crystals formed during sample preparation. Therefore, we plan to reapply for beamtime to trial improved sample holders, possibly TEM grids, silicon nitride membranes, or utilizing copper wire to conduct heat from the sample.

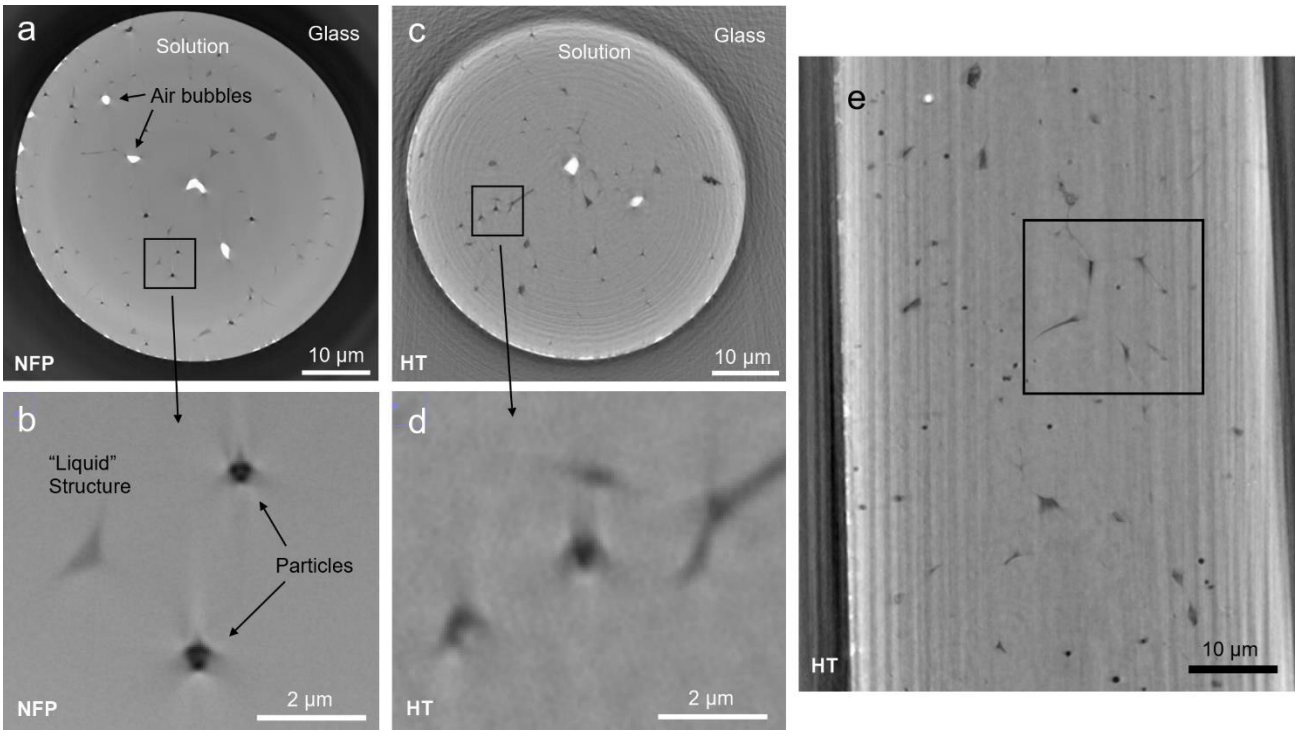

Figure 2: (a and b) 3DNFP and (c, d, and e) HT reconstructions of frozen CeOx samples in capillaries.

References: [1] Durelle *et al.*, *J. Phys. Chem. Lett.* **2022**, 8502. **[2]** Jun *et al.*, *Langmuir* **2012**, *28*, 15966.