	Experiment title: Crystallographic investigations of bassanite hydration to gypsum in the presence of additives	**Experiment number**: MA4979
Beamline: ID11	**Date of experiment**: from: 04/11/2021 to: 07/11/2021	**Date of report**: 10/09/2023
Shifts: 9	**Local contact(s)**: Carlotta Giacobbe	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Michela La Bella*, ESRF 71 avenue des Martyrs CS 40220 FR - 38043 GRENOBLE Cedex 9

Carlotta Giacobbe*, ESRF 71 avenue des Martyrs CS 40220 FR - 38043 GRENOBLE Cedex 9

Alejandro Fernandez-Martinez*, ISTerre - Maison des Geosciences Institut des Sciences de la Terre Université Grenoble-Alpes BP53 FR - 38041 GRENOBLE 9

Alexander Van Driessche, ISTerre - Maison des Geosciences Institut des Sciences de la Terre Université Grenoble-Alpes BP53 FR - 38041 GRENOBLE 9

Report:

The experiment was aimed at characterizing *in situ* the hydration of bassanite ($CaSO_4$ x $0.5H_2O$) to form gypsum ($CaSO_4$ x $2H_2O$) in the presence of additives that are commonly used in industry to produce gypsum plaster. Additives are commonly intruduced in the production process because they can modify the shape and dimensions of gypsum crystals and also tune the hydration reaction [1]. Here, our goal was to compare using phase contrast tomography (PCT) the kinetics of the dissolution of bassanite and the precipitation of gypsum due to the use of the different additives. Moreover, we also performed single crystal diffraction (SXRD) and scanning 3DXRD on single crystals of bassanite and gypsum that were prepared in the laboratory through precipitation in solutions with the same additives. Scanning 3DXRD and SXRD were used to gain information on the mosaicity of the gypsum crystals and the pseudo-merohedral twinning of bassanite [2].

- **In situ PCT experiment**

The effect of 2 additives was tested on the hydration process of gypsum plaster. Two samples were prepared. Bassanite crystals were placed inside glass capillaries with a diameter of 300 µm and hydrated *in situ*. The samples were hydrated with two solutions of 10 mM of respectively betanaphtalene sulfonate (BNS) and Polyacrylic acid (PAA). The experiment was conducted in the 3DXRD station of EH3 (one of the experimental hutches of ID11). The energy was 44 KeV. The full beam (no focusing devise used) illluminates a portion of 1 mm height of the capillaries. The projections throughout rotations of 360° were acquired with the camera Marana (2k x 2k) placed 360 mm from the sample. A pixel size of 0.63 µm was achieved using a 20x lens. After the injection of the solution in the capillaries, for each sample, a series of PCT scans were acquired for up to 24 h of hydration. The PCT scans were reconstructed using the in-house software nabu and tomwer canvas and

successively analysed with Dragonfly. Figure 1 shows the preliminary results obtained for the hydration of bassanite with a 10 mM solution of BNS. Those shown in the picture are ROIs of the capillary. The two phases, bassanite in purple and gypsum in green, were segmented using a U-Net Convolutional Neural Network implemented in Dragonfly.

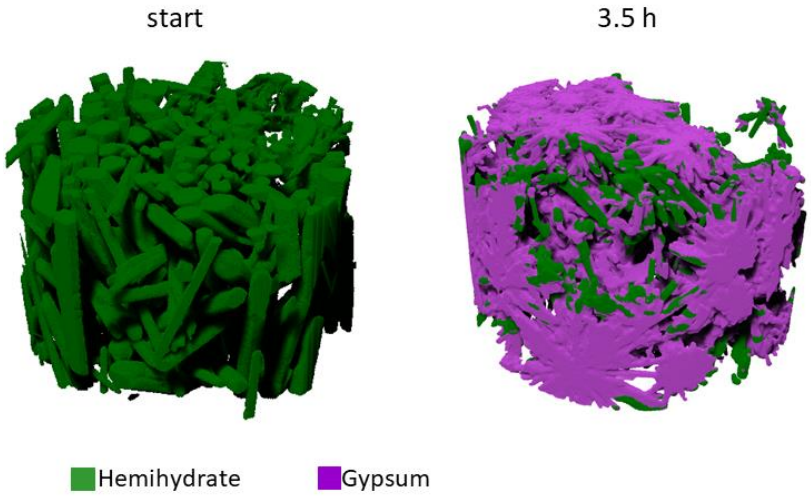

Figure 1. Preliminary results from the PCT *in situ* experiment. In this case the hydration of bassanite was performed with a 10 mM solution of BNS.

- **Scanning 3DXRD and SXRD**

Three samples of gypsum and two samples of bassanite were measured with both scanning 3DXRD and SXRD on the Nanoscope station of EH3. The crystals were mounted and glued with UV glue on Kapton loops. Figure 2 shows the images of the bassanite samples that were measured.

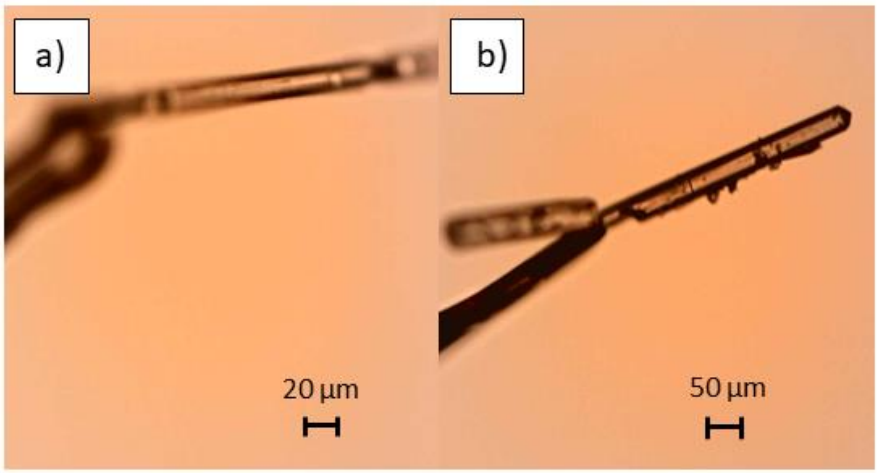

Figure 2. Microscopy images of two bassanite crystals that were measured with scanning 3DXRD and SXRD.

The energy was 44 KeV. In the case of the scanning 3DXRD measurements, the beam was focused to a size of 500 nm using Silicon compound refractive lenses. The measurements were performed acquiring one horizontal layer (x-direction) per single crystal with $\Delta x = 500$ nm and a rotation of 180° per each Δx. Figure 3 shows some preliminary results obtained from the extraction of the diffraction peaks recorded on the detector (Eiger 4M CdTe). The peaks were then used to reconstruct the sinogram (Figure 2a) and intensity map (Figure 2b) of the layer of the crystal. The preliminary data analysis was done using jupiter notebooks based on the ImageD11 software.

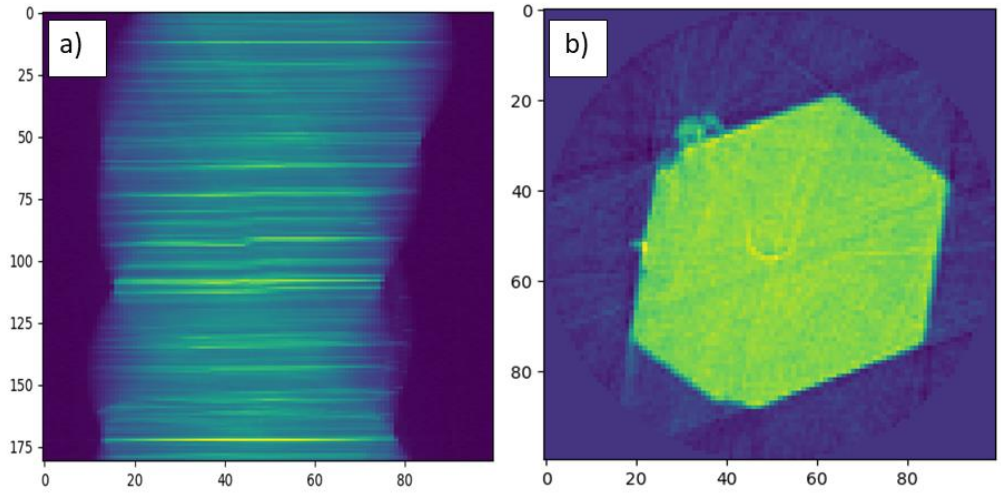

Figure 3. a) sinogram showing all the peaks collected at each angle during a rotation of 180°. b) intensity map obtained through iradon transform of the sinogram.

For the SXRD measurements, the beam was focused to a 5 µm size with Aluminum compound refractive lenses. For each crystal, a total of 1440 frames were recorded during rotations of 360° with 0.25s exposure time. Figure 4 shows the result of the preliminary analysis of the SXRD scan of one bassanite crystal. The image reports the diffraction spots of the samples in the reciprocal space. In the case of these crystals, three unit cells were identified representing the three twins of the pseudo-merohedral twinning. The preliminary data analysis has been done with the software CrysAlisPro.

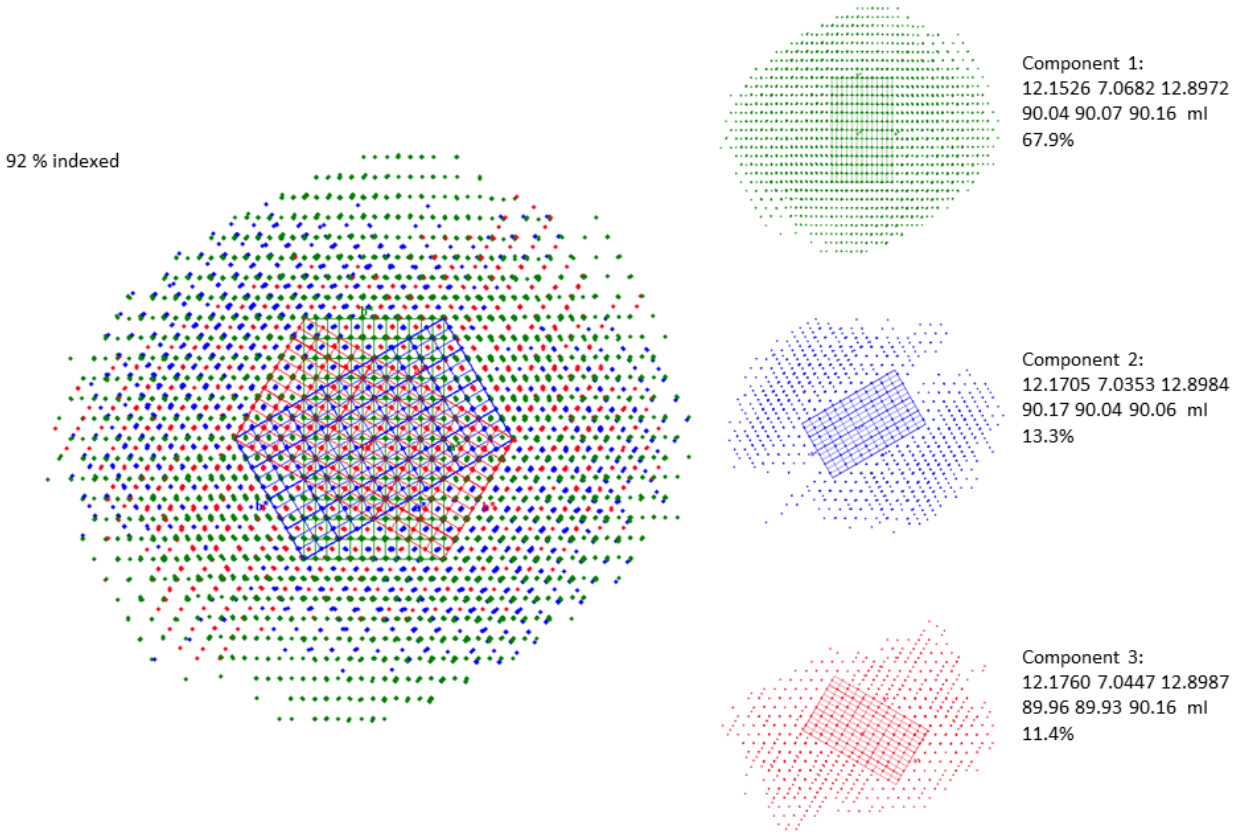

Figure 4. Diffraction peaks of one crystal of bassanite reported in the reciprocal space. The indexing procedure suggested the presence of three monoclinic I2 unit cells which is in line with the expected pseudo-merohedral twinning that is peculiar to the bassanite structure.

References:

[1] Y-W Wang, F. C. Meldrum, *J. Mater. Chem.*, 2012, **22**, 22055-22062.
[2] H. Weiss & M. F. Brau, *Angew. Chem.*, 2009, **48**, 3520 –3524.