ESRF	**Experiment title:** High Resolution Powder Diffraction of Polytype $3R_2$ Hydrotalcite	**Experiment number**: 26-01-879
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Shifts: 3	**Local contact(s)**: Dr. Wouter van Beek	*Received at ESRF:*

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Report:

Hydrotalcites (Mg-Al layered double hydroxide) are stacks of magnesium and aluminum hydroxides layers with the interlayer water and anions compensating the charges. The crystal shape is a hexagonal plate, having approximately a diameter of 200 nm and a thickness of 35 nm. Hydrotalcite can form two different polytypes, namely polytype $3R_1$ and $3R_2$. These polytypes have different layer stacking sequences, with a different interlayer spacing. Polytype $3R_2$ has a shorter interlayer distance and thus a more compact crystal structure. Polytype $3R_2$ also has a lower carbonate content in the interlayer compared to polytype $3R_1$. Due to the prefered orientation of the synthesized crystal, it is not feasible to solve its crystal structure with powder XRD. Since a single crystal of polytype $3R_2$ is not available, the combination of narrow peaks, accurate reflection positions and intensities is essential for Rietveld refinement from powder diffraction data. The aim of this experiment is to acquire measured high resolution p-XRD patterns in order to solve the crystal structure of polytype $3R_2$.

For crystallographic studies, the use of a spinning capillary essentially eliminates preferred orientation effects of the sample [2]. Three samples were measured by high resolution powder diffraction in beamline BM01B. The specimens were contained in capillaries with 0.7 mm diameter and 0.01 mm wall thickness. During the measurement, the capillaries were spinned. The wavelength was 0.50109 Å. The 2θ-range was 1.5–40° with a step size of 0.003° and a counting time per step of 0.5 s. Additional measurements were carried out in beam line BM01A with an image plate detector mar345. The wavelength of the measurement was 0.7000 Å. The detector was placed 200 mm from the specimen. During the measurement, the sample holder was rotated 1°/sec. The exposure time was 120 sec.

Figure 1 showed that indeed that synchrotron HRPD measurement reduced the preferred orientation effect. Owing to the platelet shape of the crystal, the measurements with CuKα radiation which was carried out from a thin layer specimen showed high degree of preferred orientation on the basal (00l) reflections. As

layered material, LDH are prone to stacking faults which could result to broadening of the reflections, the synchrotron measurement were also expected to give a narrower reflection which could reveal possible overlapping reflections, especially those of polytype $3R_1$ in the basal reflections. However, the synchrotron measurement did not reveal additional reflections compared to the CuKa measurement, indicating that should there be presence of $3R_1$ in the sample, it is possibly manifested as stacking faults.

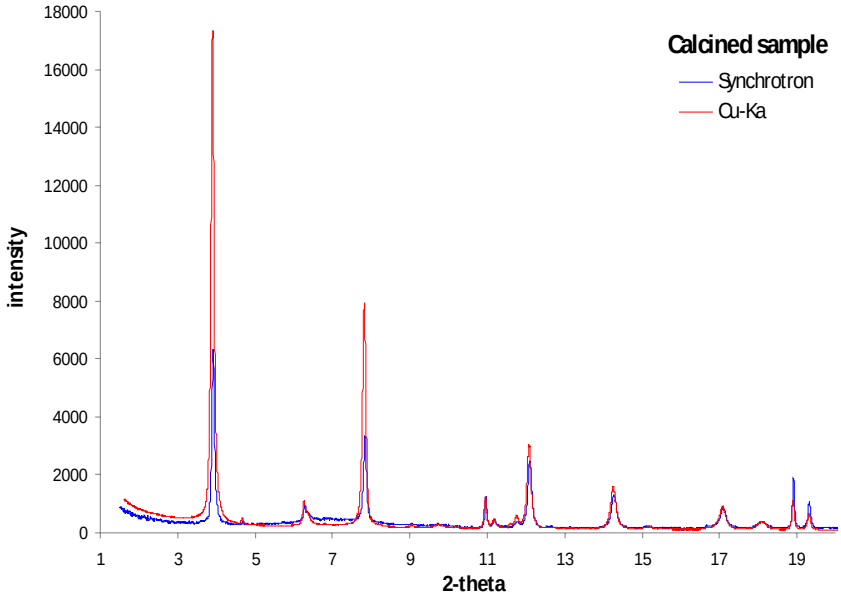

Figure 1. p-XRD measurements of sample 1 by synchrotron radiation and CuKα radiation.

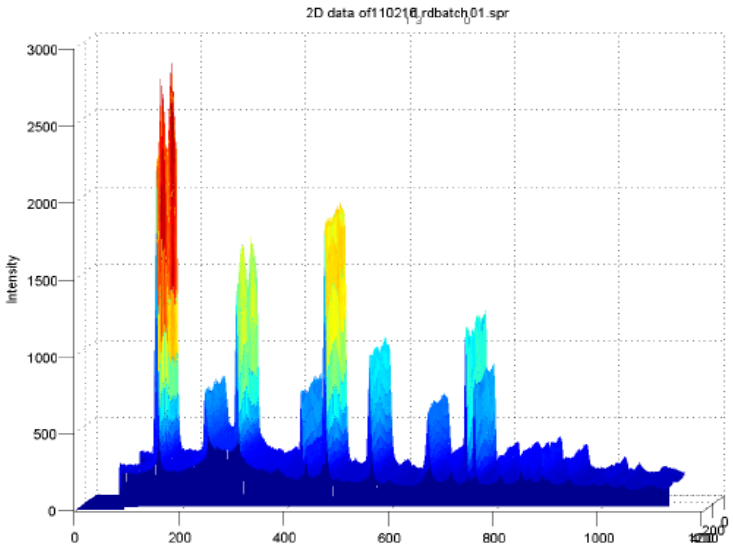

Figure 2. Diffractogram of sample 1 at various azimuth angles measured with MAR345

Shown in Figure 2 is the 2D diffraction image measured at 360 degrees azimuth angles of sample 1. Observation of the image shows that the preferred orientation of this specimen still exist in the *(003)* and *(006)* reflection although they are not major, as the intensities of each line seems to be similar. The similar measurement carried out for the other samples, however showed that the specimens showed more preferred orientation on both the basal and non basal spacing (picture not shown). In the HRPD setup, it was only possible to carry out the measurements for a single azimuth angle. For that reason, the HRPD pattern of sample 1 which have the least preferred orientation is the most suitable one for the Rietveld refinement.

References

[1] Newman, S.P., Jones, W., O'Connor, P., Stamires, D.N. 2002. *Journal of Materials Chemistry* **12**: 153-155.

[2] Fitch, A.N. 2009. *J. Res. Natl. Inst. Stand. Technol*. **109**: 133-142.