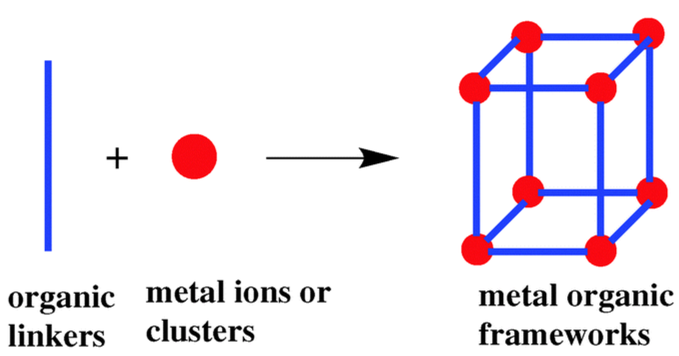
Thin Film Analysis of Copper Based Metal-Organic Frameworks

M. Fratschko[(1)], M. Linares-Moreau[(2)], M. Velasquez Hernandez[(2)], M. Kaltenegger[(1)], A. James[(1)], P. Falcaro[(2)] and R. Resel[(1)]

[1] *Institute of Solid State Physics, Graz University of Technology, Austria*
[2] *Institute of Physical and Theoretical Chemistry, Graz University of Technology , Austria*

Introduction

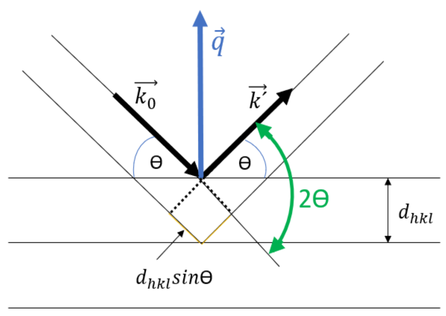
A Metal-Organic Framework (MOF) is a porous regular structure, build up from some metallic ions or clusters, which get connected with some organic linker material. Since any metallic cluster and organic linker can form a MOF when they combine, there are a large number of possible combinations, resulting in a very diverse class of materials. Furthermore, the properties of the MOFs can be precisely tuned by the appropriate metal centers and organic linkers. The length of the organic linker, for example, directly changes the size of the pores in the resulting materials, while the metal cluster determines the geometry to which the linker attaches. [1]
The idea of this project is to prepare oriented thin film MOF structures from solution in order to further develop a methodology for crystal structure solution, and to apply this method to unknown polymorphs. The MOF selected for this first analysis is copper-benzene-dicarboxylate (Cu(BDC) or SURMOF-2).



Schematic presentation of the formation of a Metal-Organic Framework

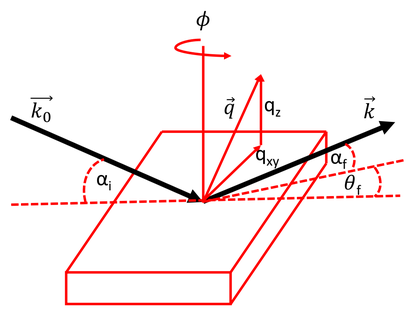
Experimental I

Specular X-ray diffraction experiments were performed on the in-house Panalytical setup with a X-ray wavelength of 1.54 Å. X-ray diffraction occurs acording to Bragg´s law (nλ = 2d*sin(θ)) and the angle of the incoming and outgoing beam are the same, thus the scatttering vector is perpendicular to the substrate surface.



Geometric principle of Bragg´s law

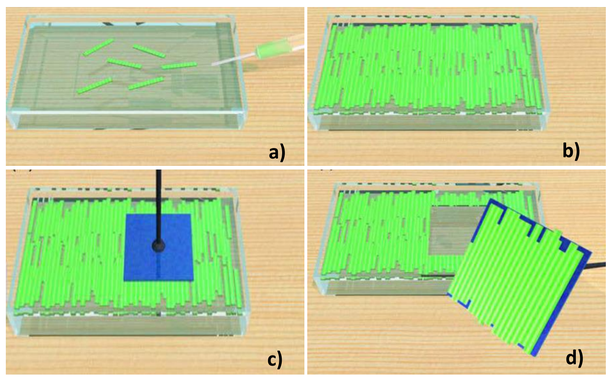
Experimental II



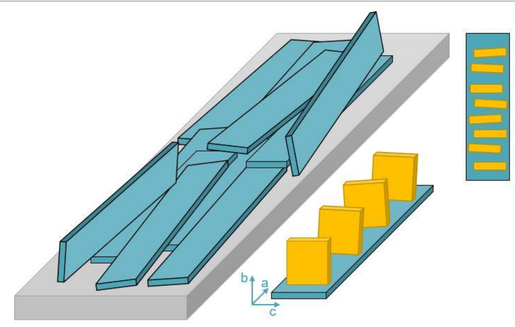
Basic pronciple of GIXD

Gracing Incidence X-Ray Diffraction is a surface sensitive method with a small angle of the incoming beam, which is in the range of the critical angle. Below the critical angle, there is total reflection and instead of X-rays, the diffraction of an evanescent wave, generated on the surface, is detected. By additional rotation of the sample the whole diffraction information can be obtained. The measurements were performed in Elettra, in Trieste, on the XRD1 beamline with a wavelength of 1.4 Å.

Preparation

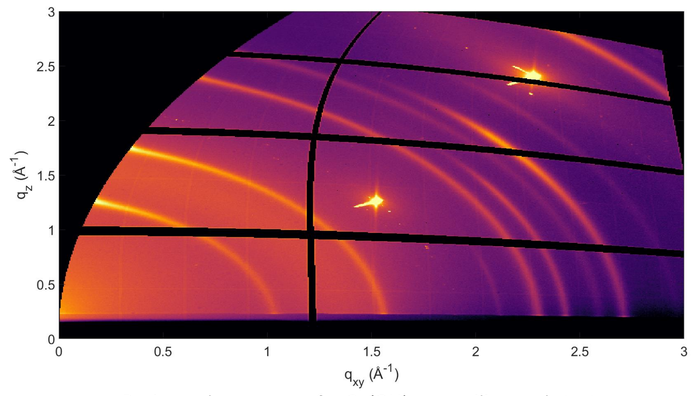


The synthesis of Cu(BDC) is performed in 2 steps. First, $Cu(OH)_2$ nanobelts are deposited on top of a silicon substrate. For this purpose the $Cu(OH)_2$ nanobelts were synthesized following a reported procedure and afterwards dispersed in ethanol. Afterwards, the dispersed nanobelts were injected on a water surface using a syringe. Finally, a silicon substrate was manually pressed on the nanobelt film with a quick motion to remove it from the water. This nanobelts act as a template for the formation of an oriented MOF. Second, for the conversion to the MOF, the crystalline $Cu(OH)_2$ nanobelts are exposed to the ethanolic solution of the ligand, where $Cu(OH)_2$ releases Cu^{2+} cations, which are rapidly linked by the ligand. Within minutes, crystalline Cu(BDC) forms and its lattice is precisely aligned to the lattice of the $Cu(OH)_2$ nanobelts. [1]

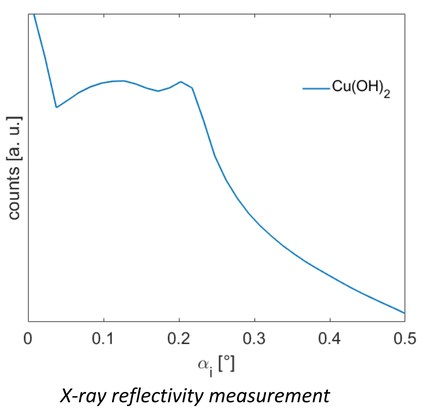


Visualization of the oriented Cu(OH)2 nanobelts in one direction (blue) on the silicon substrate (grey). The Cu(BDC) MOF (yellow) is forming on top of the nanobelt.

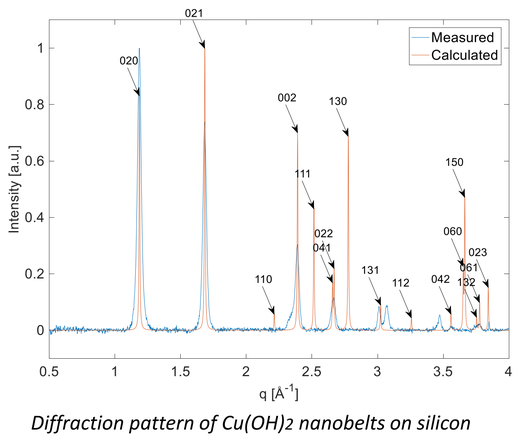
Results I ($Cu(OH)_2$)



Reciprocal space map for $Cu(OH)_2$ on a silicon substrate



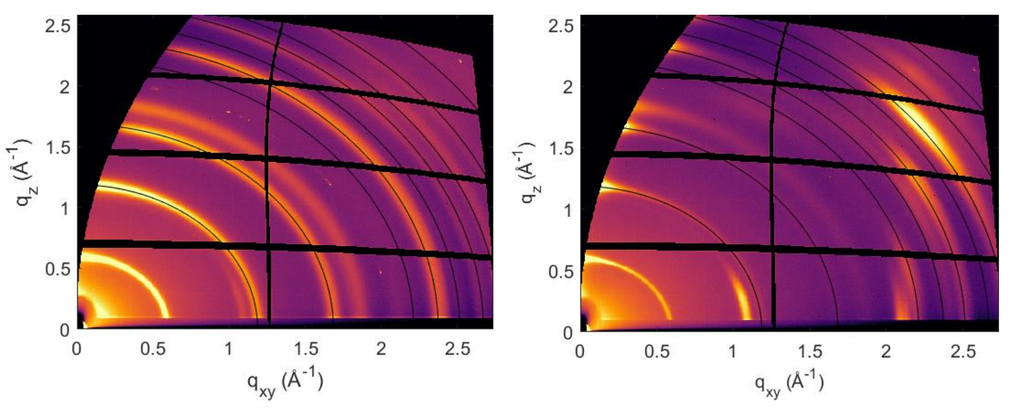
X-ray reflectivity measurement



Diffraction pattern of $Cu(OH)_2$ nanobelts on silicon

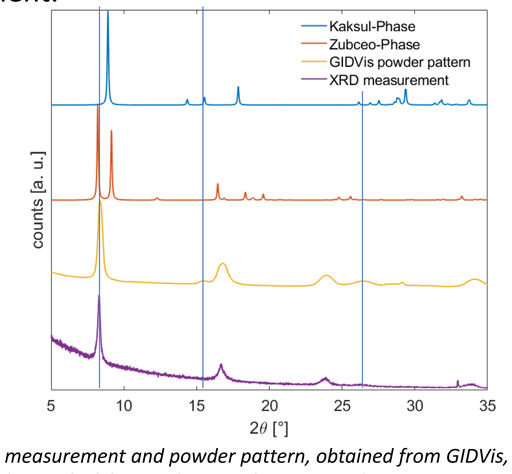
The GIXD map of $Cu(OH)_2$ is needed to distinguish the Cu(BDC) peaks from the Cu-nanobelt peaks.
An XRR scan was performed to determine the critical angle ($\alpha_c = 0{,}2822\ °$) of the nanosheets. From this, the electron density was calculated which is ($\rho_e = 1{,}13956\ \frac{1}{Å^3}$).
The diffraction pattern shows us that there are only (0kl) reflexes, which means that the nanobelts are aligned with an axis along the substrate.

Results II (Cu(BDC))



Reciprocal space map for Cu(BDC). The left map shows the diffraction signal of the substrate at a rotation of 35 degrees, where the right map shows the diffraction signal at a rotation of 125 degrees. The black lines indicates the diffraction of $Cu(OH)_2$.

By comparing the two reciprocal space maps an in plane ordering of the MOF is visible. Indexing the reciprocal space map with two known phases for Cu(BDC) showed no match. This means that a different phase occurs when the MOF is prepared with a solvent. There is also no agreement when comparing the two known phases with the powder sample from GIDVis and the XRD measurement.



Comparison of the XRD measurement and powder pattern, obtained from GIDVis, of Cu(BDC) with the known phases of Kaksul and Zubceo. Black lines indicating the measured MOF.

Conclusion and Outlook

The experimental data gives us information about the texture of the $Cu(OH)_2$ nanobelts and Cu(BDC) MOF. Also the crystal structure can be calculated out of the GIXD maps. Thus the next step is the structure determination of Cu(BDC). In addition to Cu(BDC), three other MOFs were measured at the synchrotron for which structural analysis must also be performed.

This work was supported by the Austrian Science Foundation (FWF) [grant number P34463]
Corresponding author: mario.fratschko@tugraz.at

References:
[1] M. Linares-Moreau, et al., Advanced Materials Interfaces (2016)