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For Poster Presentation

On Substitution Tilings with n −Fold Dihedral Symmetry and Non-Pisot Substitution Factors, $n \in \{13, 17, \ldots, 37\}$

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We present an approach that facilitates the construction of a substitution whose hull contains an individual substitution tiling $\mathcal{T}_n$ with n −fold dihedral symmetry, for $n \in \{13, 17, 21, \ldots, 37\}$. The existence of a substitution tiling with 17-fold dihedral symmetry is exhibited.

The substitution factor is $\mu_n = \sin\left(\frac{(n-1)\pi}{2n}\right) / \sin\left(\frac{\pi}{n}\right)$, which is non-Pisot.

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Determination of Instrumental Broadening

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Both, the instrument and the sample contribute to the XRD peak broadening. To calculate the effect of the sample, be it crystallite size or microstrain, the instrumental broadening is needed. Therefore, we determined the instrumental broadening as a function of 2θ of the Bruker D2 phaser. As sample material we used powdered silicon and lanthanum hexaboride, whose crystallite size was sufficiently large for no broadening effect to occur (>1 µm). X-ray diffractograms from 20 – 140° 2θ with a step size of 0,002° were recorded. Peak profiles were fitted and Full Width at Half Maximum (FWHM) and integral breadth values were calculated for each peak (Bruker software EVA). The evaluation was performed according to Scherrer (FWHM) and according to Laue (integral breadth) [1]. It was possible to determine the instrumental broadening as a function of 2θ of the silicon and lanthanum hexaboride diffraction patterns (see Figures 1 and 2). Since the peak width caracteristic of both sample materials awere found to be congruent, a very good agreement can be found between the two materials, both for the integrated width and for the FWHM, a possible influence of microstrain can be excluded.

Figure 1. Instrumental Broadening, determined with integral breadth on LaB6 and Silicon

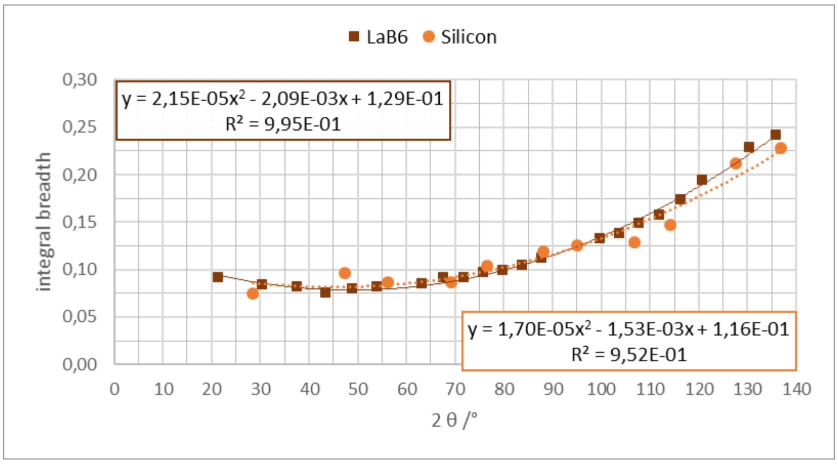
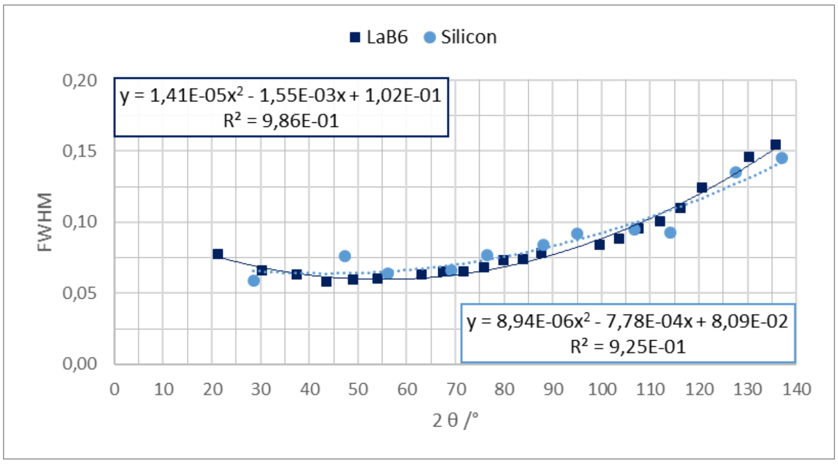


Figure 2. Instrumental Broadening, determined with full width at half maximum on LaB6 and Silicon



To determine the sample caused peak broadening of any other sample, the known instrumental breadth can now be subtracted from measured breadths. According to the Williamson-Hall plot method, we separate the effects of crystallite size and microstrain using the equation $\beta = \frac{K\,\lambda}{d\cos\theta} + 4\varepsilon\tan\theta$ where β is the sample caused peak broadening, K a form factor, λ the wavelength, d the crystallite size and ε the microstrain. $\frac{K\,\lambda}{d\cos\theta}$ represents the size effect, $4\varepsilon\tan\theta$ the strain effect [2-3].

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Revisiting rules on (un-)striated surfaces and twinning: FeS_2 and $CaCO_3$´s case studies

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Crystal shapes and surfaces depend on known thermodynamical and kinetical processes, while twinning and co-growing still present a challenge to understand the consistency at the microscopic and macroscopic scales. This study combines atomistic simulations and experimental observations. The striated texture observed on natural minerals can correspond to a unidirectional or bidirectional kinetical growth and the inspection of striations becomes an important tool to recognize laws in co-grown and twinned crystals. For example, the marcasite FeS_2 (101) surface is structurally and energetically similar to the pyrite (001) (Surface energies of 1.06 J/m^2 and 1.04 J/m^2 respectively, with force field simulations) and the epitaxial relationship between them favours the co-growth in a specific orientation following the surface sulphur alignments (visible on STM images simulated with DFT). The striated [001] direction of marcasite enables as well to spot (101) mirror twins, energetically stable. Another interesting result is that the striations onto pyrite surfaces bring new insights in distinguishing {201} pyritohedron from {102}, the latter being stabilized under geothermal conditions, and in distinguishing their iron-crossed twins, being a rotational $[001]_{90°}$ twin [1,2]. The macroscopic twinning rules are dominated by the cation network and the stability of the grain boundaries is due to stable and clean interfaces. Similar observations can be done on $CaCO_3$ polymorphs. In the case of biomineralization processes, another phenomenon can be highlighted: the self-assembly of small particles, obeying to rotational twinning laws to form pentagonal and hexagonal superstructures (unpublished results).

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Structural Study of Organic Cocrystals Using 3D Electron Diffraction

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One of the main limitations on the effectiveness of Active Pharmaceutical Ingredients (APIs) is their low solubility in water resulting in low oral bioavailability. To improve this, one of the proposed solutions is cocrystallization with compounds known as Generally Recognized As Safe (GRAS) [1]. APIs cocrystals are composed of two molecules in the same lattice bonded by noncovalent bonds[2].

This work addresses the structural study of oxyresveratrol cocrystals formed by mechanosynthesis. Ethyl maltol, isonicotinamide, urea and nicotinamide were used as GRAS coformers.

Mechanosynthesis often leads to the formation of crystals too small for single-crystal x-ray diffraction (SCXRD) hence finding structural information is an extremely hard task.

3D electron diffraction is the most suitable to solve this task with some unique advantages in the analysis of small crystals. In 3D ED single crystal diffraction data of structure solution quality can be collected on grains as small as few hundreds of nanometers[3,4,5]. Thanks to a new generation of single electron detectors this kind of experiment can be performed in low dose, therefore beam sensitive crystals like organics do not amorphized during the duration of the experiment. With the knowledge obtained from the crystal structure, modifications can be made during the intermediate crystallization steps or to the final compounds which can be crucial for the commercialization of APIs.

Our preliminary results show changes in the unit cell parameters of the newly formed cocrystals with respect to their initial precursors which indicate that the process of cocrystallization was achieved.

PXRD has been performed to cross-check the structure derived with electrons diffraction. Despite submicrometric crystals size and a strong stacking disorder their unit cell parameters were successfully determined and used for further crystal structure elucidations.

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Synthesis, crystal structure and Hirshfeld surface analysis of a new coordination complex with 3-aminopyridine

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Recently aminopyridine ligands have been widely studied in the synthesis of many coordination metal compounds spanning from simple mononuclear, dinuclear complexes to coordination polymeric compounds (CPs) with varying dimensionality **[1],** 3-Aminopyridine (3-ampy) as one of the aminopyridine series is a simple molecule. Like other amino-substituted pyridines 3-aminopyridine (3-Apy) has potential electron donor nitrogen atoms which can act as mondentate ligand by binding the metal ions in the most common binding mode via the most basic N-pyridyl nitrogen which is attributed to the stronger basicity of pyridine nitrogen **[2],** or the least likely binding site of the amino group to coordinate metal ions and serve as useful ligand in a variety of inorganic and organometallic applications **[3]**. Moreover, the molecule can also, simultaneously bridging two metal ions via the N-pyridyl and N-amino donor atoms.

During our investigation we synthesized a new coordination complex with (3-Apy) and Cadmium nitrate. The coordination complex has been characterized by single crystal X-Ray diffraction. The structural study showed that the complex crystallises in the monoclinic system in the $P2_1/n$ space group. To get a better insight into the molecular interaction we conducted the Hirshfeld surface analysis.

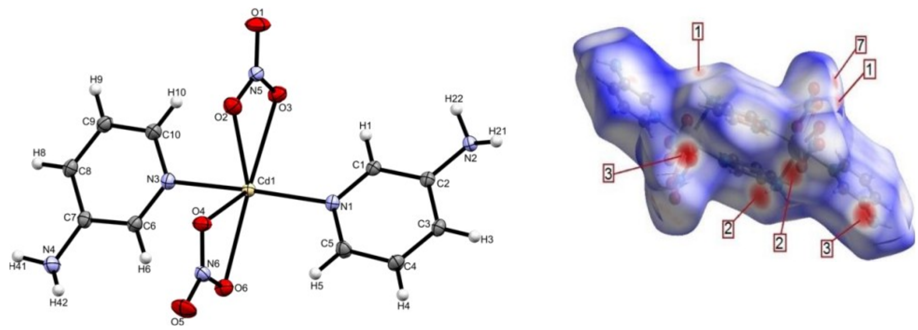

Fig.1 Asymmetric Unit and Hirshfeld Surface (mapped over d_{norm}) of $[Cd(3\text{-}Ampy)_2(NO_3)_2]_2$

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Iron based Chalcogenide $BaFe_2S_3$

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Unconventional superconductivity (SC) and magnetism are usually mutually exclusive. However, magnetic order seems a necessary foe of unconventional SC. It is particularly the case in cuprates (AFM order in the vicinity of the SC state) or Fe-based SC (spin density wave close to the SC state). The current obstacles in the understanding of Cooper pairing mechanism are related to the dimensionality of the systems. Considering quasi-1D systems should be much simpler and should lead to the emergence of new theoretical models. Fe-based spin-ladders of the type $BaFe_2X_3$ (X=S, Se) are particularly interesting quasi-1D compounds. They are insulators at room temperature and ambient pressure. In addition, $BaFe_2Se_3$ is ferrielectric at 300K. Below TN (250 K for $BaFe_2Se_3$ and 120 K for $BaFe_2S_3$), a magnetic order develops along the spin ladders resulting in multiferroic property. The magnetic and dielectric behaviours are strongly different in the two types of spin-ladders which is not yet understood. Under pressure, a SC transition occurs in both systems leading to a very rich phase diagram as a function of pressure and temperature. The influence of other external parameters, such as magnetic/electric fields, charge doping, chemical substitution or ionic irradiation remains to be investigated with a reasonable hope to discover new phases, new properties and a better understanding of theses materials. Indeed, each of these parameters is likely to favor one or another instability among the many orders present in this family. By destabilizing the fragile balance between the different underlying order parameters, we expect to reach new remarkable ground states. This is the objective of my PhD. To study this family, we use a large range of experimental techniques: X-ray diffraction (atomic structure), IR (phonons).

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Crystalline phases in the magnesium sulphate-urea-water ($MgSO_4$-CH_4N_2O-H_2O) system

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This work presents results of our study of the $MgSO_4$-CH_4N_2O-H_2O system. The purpose of the present study is to determine the conditions for the preparation in pure form of the known urea complexes of magnesium sulfate and their spectral and thermal characteristics. Since for two of the phases in the system, $MgSO_4.OC(NH_2).2H_2O$ and $MgSO_4.OC(NH_2).3H_2O$, we were unable to find information on their crystal structures, so single crystal samples were obtained for these compounds and the crystal structures determined.

In the system there are four different compounds: $MgSO_4.6OC(NH_2).0.5H_2O$[1] ; $MgSO_4.4OC(NH_2).H_2O$[2] ; $MgSO_4.OC(NH_2).2H_2O$[3] ; $MgSO_4.OC(NH_2).3H_2O$[4]. The structural parameters of the studied compounds are presented in **Table 1** and the structural units, building the crystalline structures are visualised on **Figure 1**.

The crystal structure comparison shows that the number of ligands (urea and water), determines the dimensionality or type of structural units. In ***1*** and ***2*** there are isolated octahedral units connected by hydrogen bonds, in ***3*** a layer of interconnected octahedra of different types is formed, and in ***4*** - a chain of identical octahedra.

Figure 1. Crystalline structures in the $MgSO_4$-CH_4N_2O-H_2O system

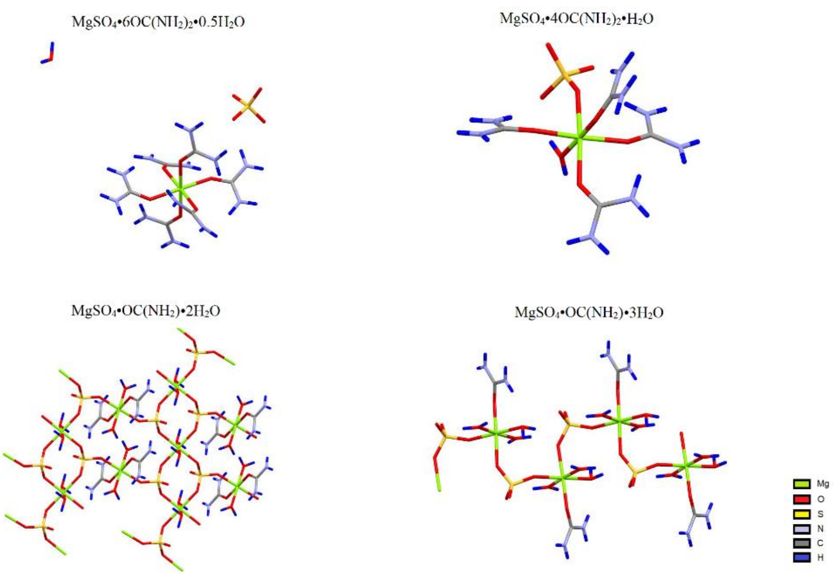

Table 1 Structural parameters of the studied compounds

Formula	Space Group	Cell lengths			Cell Angles			Cell Volume
		a	b	c	α	β	γ	
$MgSO_4$•$6OC(NH_2)$•$0.5H_2O$	P c c n	15.316(5)	19.798(5)	14.484(2)	90	90	90	4391.93
$MgSO_4$•$4OC(NH_2)$•H_2O	P 2_1/n	9.345(2)	4.683(4)	11.244(3)	90	93.07(2)	90	1540.6
$MgSO_4$•$OC(NH_2)$•$2H_2O$	P -1	5.211(5)	7.694(8)	10.435(11)	68.60(3)	77.03(3)	71.51(3)	366.611
$MgSO_4$•$OC(NH_2)$•$3H_2O$	P 2_1	5.2474(12)	7.7075(14)	10.231(2)	90	94.261	90	412.642

High-pressure/temperature single crystal X-ray diffraction at the Partnership for eXtreme Xtallography (PX2) Program

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Single crystal X-ray diffraction is an established method to constrain the structure and chemistry of crystalline minerals under extreme conditions. PX2 is a high-pressure/temperature crystallographic research program dedicated to diamond anvil cell research. Located at the experimental station 13-BM-C of the Advanced Photon Source, PX2 provides 10 μm-level focused X-rays at a fixed energy of 28.6 keV, a 6-circle heavy duty diffractometer and a state-of-the-art Pilatus3 1M photon-counting detector, optimized for a variety of advanced crystallography experiments. A suite of auxiliary equipment including a compact multipurpose optical table and remote membrane-based pressure control has been installed to facilitate the experiments. Resistive and laser heating capabilities have been commissioned to provide high temperature sample environments for the study of the planetary interior. In this poster we present a few examples to demonstrate the experimental capabilities at PX2.

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Ionic moduli: A new semi-empirical model for the elasticity of crystalline ionic compounds

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The compressibility of a material (or its reciprocal, the bulk modulus) is a fundamental parameter governing the behavior of materials at non-ambient conditions, but there currently exists no quantitative model explaining the bulk modulus of a material in terms of simpler parameters. A novel, semi-empirical model is presented which quantitatively predicts the bulk modulus of a crystalline ionic compound in terms of the compression of its constituent ions. The model assumes that ions are elastic spheres which compress reproducibly and independently of their environment, according to a simple first order equation of state. These ionic moduli (defined analogously to the bulk modulus) are then combined via a Reuss-style limit to give the bulk modulus of the material. Testing this model against P-V compression data for the alkali halides (all with B1 or B2 cubic structures) reveals that the model correctly predicts the bulk moduli of strongly ionic compounds within 10% error, much better than expected by statistics alone given the number of model parameters. It is also demonstrated that the compressibility of most alkali metal and halide ions are a simple linear function of the zero-pressure ionic radius. The results indicate that electron clouds compress in a largely reproducible fashion according to a simple physical law relating to the radial distribution of electrons.