New high pressure X-ray powder diffraction capabilities at the SLS-Material Science Beamline

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The Swiss Light Source Material Science (SLS-MS) beamline powder diffraction station has been recently equipped with a gas-driven diamond anvil cell for *in-situ* non-ambient high pressure X-ray powder diffraction investigations. First experiments have been conducted to investigate the structural behavior of organic and metal-organic compounds at non-ambient conditions.

High pressure XRPD equipment at SLS-MS Beamline Powder Station

A gas-driven Boehler-type membrane diamond anvil cell is now available at the SLS-Material Science Beamline to perform high pressure X-ray diffraction experiments. The Boehler-type DAC has a large angular aperture (85°) that allows conducting high d-spacing resolution XRPD measurements. Non-ambient pressure up to 30 GPa can be reached with 500 µm diameter diamond culets with the pressure driven via a gas-membrane mechanism (Figure 1). Regulated by an attached gas line, the pressure can accurately be risen in small steps (0.1-0.2 kbar). Diffraction data are recorded using MYTHEN II detector [1]. Type IIa diamonds have been mounted, which are also suitable for in-situ high pressure infrared (IR) experiments. SR-XRPD and IR experiments can, therefore be performed under the same identical experimental conditions at the SLS-MS powder diffraction and SLS-IR spectroscopy beamlines. At this purpose, special attention has been paid to the geometry of the cell and the overall experimental set up so to not only fit both beamlines but also achieve a user-friendly swap between them. High pressure XRPD capabilities will be extended in the upcoming months by a gas-driven high temperature diamond anvil cell. The possibility of combined high temperature/high pressure experiments will be particularly interesting to probe the non-ambient structural behavior of pharmaceutical compounds. This includes crystallization experiments in the diamond anvil cell, applying temperature gradients in isobaric conditions. Complementary single crystal high pressure XRD can be performed at the Laboratory for Chemical Crystallography at the University of Bern, using a screw driven DAC working in a pressure range 0-10 GPa

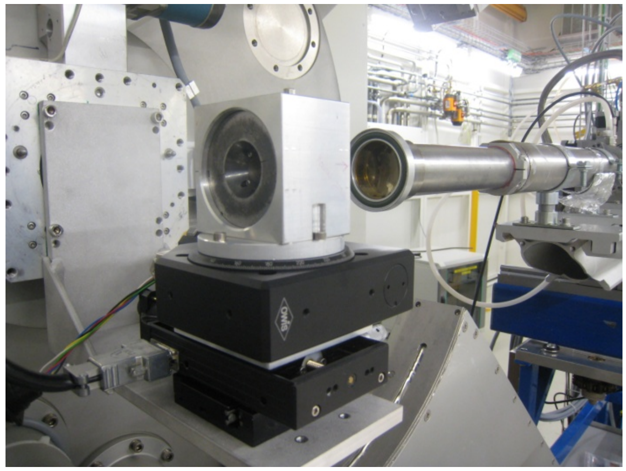

Figure 1: Boehler-type diamond anvil cell for at SLS-MS Beamline Powder Station

First experiments and results

We have undertaken some preliminary studies using the new equipment at the SLS-MS beamline on a rather large variety of subjects: a) structural behavior of metal organic frameworks (MOF) under high pressure; b) pressure induced changes of transition metal carbonyls; c) structure property correlation of organic non linear-optic active species; d) search of polymorphic forms of pharmaceuticals. We briefly report on the study of Zeolitic imidazolate frameworks, an interesting class of MOF's.

Zeolitic imidazolate frameworks and ZIF-4

Zeolitic imidazolate frameworks (ZIF's) are porous materials that form open framework structures by linking transition metals ions (Zn, Co) and the organic molecule imidazole and find applications in gas-separation, gas-storage, and heterogeneous catalysis. ZIF's are of particular interest because of their remarkable chemical and thermal stability [2]. Traditionally, these materials have been exposed only to very moderate pressures. An understanding of the behavior of metal organic frameworks under high pressure could give information on the mechanical properties of these materials and therefore lead to more advanced engineering and applications. So far, there has been only very few X-ray diffraction studies of metal organic frameworks under high pressure using diamond anvil cells.

The scope of this study was to investigate the structural response of the zeolitic imidazolate framework to elevated hydrostatic pressure in relation to potential phase transition, pressure induced amorphization and subsequent recrystallization. ZIF-4 $[Zn(Im)_2]$ was selected as a candidate for reversible amorphization, because amorphization of the framework was observed during thermal treatment [3]. The use of a pressure medium during high pressure experiments that is commonly employed to ensure hydrostatic pressure conditions, allowed us, in the case of the ZIF-4 system, to also probe the framework stability in relation to the presence of guest- and solvent molecules. Two types of pressure media have been used for this purpose: 4:1 methanol:ethanol and Daphne oil. Methanol is small enough to interpenetrate the framework, while Daphne oil (a type of mineral oil) is too large to enter the structure (Figure 2). To probe the effect of the pressure medium on the structural stability of ZIF-4 under high pressure, the following 4 experiments were carried out:

1) ZIF-4 as synthesized (containing DMF solvent molecule) using 4:1 methanol:ethanol
2) ZIF-4 as synthesized (containing DMF solvent molecule) using Daphne oil
3) ZIF-4 evacuated using 4:1 methanol:ethanol
4) ZIF-4 evacuated using Daphne oil

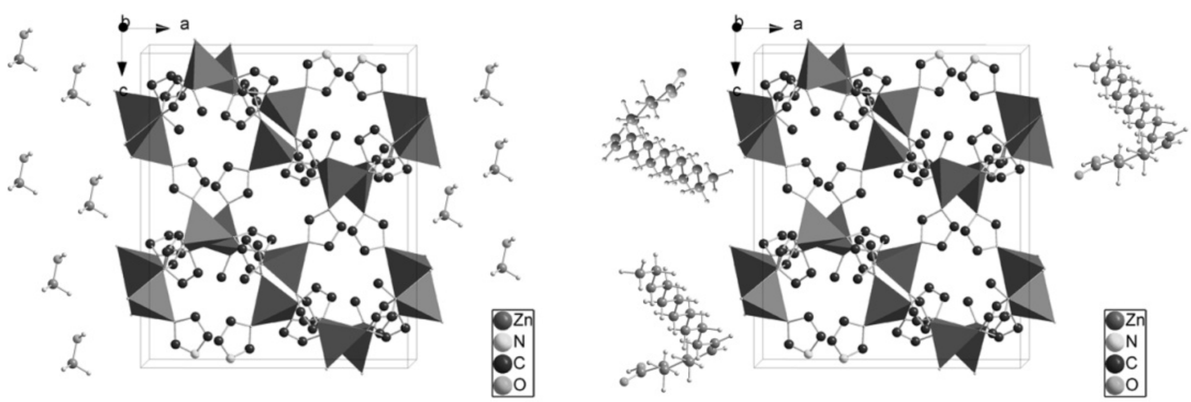

Figure 2: ZIF-4 and the pressure medium methanol (left) and Daphne oil (right)

Pressure induced amorphization occurred independent of the presence of a solvent molecule or the pressure medium used. However the pressure at which the amorphization occurred was significantly influenced by the presence of an interpenetrating guest molecule from the pressure medium. Using 4:1 methanol:ethanol as a pressure medium, crystalline features were present up to at least 40 kbar. Even at 75 kbar the sample appears not completely amorphous. Using Daphne oil as a pressure medium, amorphization started to set in at 5 kbar and the sample was entirely amorphous at 26 kbar. Independent of the pressure medium used, all samples showed recrystallization once the pressure was released to ambient conditions. High pressure phases were observed depending on the presence of the solvent molecule. ZIF-4 containing the DMF solvent molecule displays a orthorhombic $P2_12_12_1$ and a monoclinic $P2_1/c$ phase at high pressure. An orthorhombic-orthorhombic phase transition was observed in the evacuated ZIF4, while the monoclinic phase was absent.

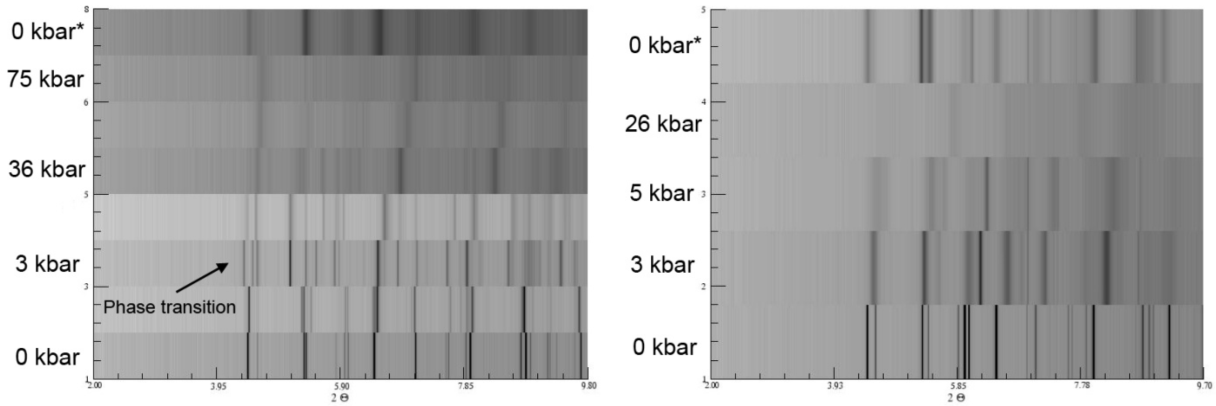

Figure 3: High pressure powder diffraction data of evacuated ZIF-4 using methanol (left) and Daphne oil (right). 0 kbar* shows the recrystallization after pressure release. (1 GPa = 10 kbar).

Solvent present	Hydrostatic Medium	Phase transition (GPa)	Amorphization (GPa)
Yes	Daphne oil	0.21-0.32	2.61 – 6.43
Yes	4:1 Methanol:ethanol	0.00 – 0.12	2.02 – 4.53
No	Daphne oil	0.17 - 0.35	0.35 – 0.98
No	4:1 Methanol:ethanol	0.05 - 0.79	0.25 – 0.48

Table 1: Summary of synchrotron high pressure powder XRD investigating ZIF-4

The reversible pressure-induced amorphization of a Zeolitic Imidazolate Framework (ZIF-4) has been reported for the first time, as also observed in zeolites and aluminophosphates [4, 5].

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