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## Experimental Evidence of Negative Linear Compressibility in the MIL-53 Metal-Organic Framework Family

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**We report a series of powder X-ray diffraction experiments performed on the soft porous crystals MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al) in a diamond anvil cell under different pressurization media. Systematic refinements of the obtained powder patterns demonstrate that these materials expand along a specific direction while undergoing total volume reduction under an increase in hydrostatic pressure. The results confirm for the first time the Negative Linear Compressibility behaviour of this family of materials, recently predicted from quantum chemical calculations.**

A special class of metal organic frameworks (MOFs) are those whose pore dimensions change upon external stimuli, the so-called soft porous crystals (SPCs).<sup>1</sup> In SPCs, adsorption and desorption of different molecules, changes in temperature or even mechanical pressure result in different phenomena like the breathing effect and the gate-opening effect, where pores contract or expand as a response.<sup>2-4</sup> One of the most studied SPCs is the MIL-53 family, built from M(OH)<sub>2</sub> octahedra (M being Fe<sup>3+</sup>, Al<sup>3+</sup>, Ga<sup>3+</sup>, Cr<sup>3+</sup>, In<sup>3+</sup> or Sc<sup>3+</sup>) and terephthalate ligands, resulting in one-dimensional pores with diamond-shape and unit cell changes from approximately 1500 Å<sup>3</sup> to 1000 Å<sup>3</sup>.<sup>5, 6</sup> The large difference in pore volume is attributed to the so called breathing effect. MIL-53(Al) is well known to undergo a phase transition from the large pore (*lp*) phase (pore volume of around 1500 Å<sup>3</sup>) in the absence of adsorbate to a narrow pore (pore volume of around 1000 Å<sup>3</sup>) when exposed to certain molecules like water and carbon dioxide.<sup>7</sup> In the case of the amino functionalized version of MIL-53, the evacuated material shows a very narrow pore (*νnp*) phase in vacuum (pore volume ca. 940 Å<sup>3</sup>). When exposed to different adsorbates, the NH<sub>2</sub>-MIL-53(Al) frameworks expands first to a narrow pore *np* phase (pore volume of

around 990 Å<sup>3</sup>) and to a *lp* phase at higher adsorbate pressures (pore volume of 1450 approx.).<sup>8</sup>

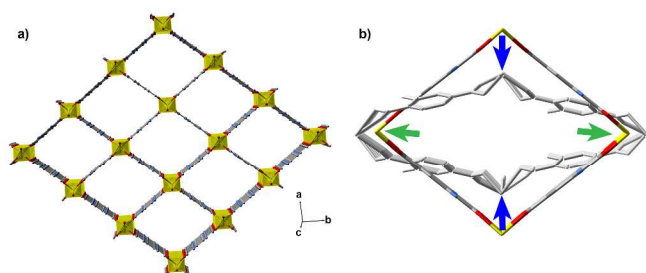
As the interest in MOFs grew over the last two decades, several researchers have studied their thrilling mechanical properties: elastic behaviour, hardness, pressure-induced amorphization and pressure-induced structural transformations.<sup>9-15</sup> When it comes to SPCs, Beurroies *et al.* were able to induce the phase transition from the *lp* to the *np* configuration on MIL-53(Cr) by using external pressure.<sup>16, 17</sup> More recently, we reported the high amorphization resistance (> 20 GPa) and large compressibility ( $K_0 = 10.9$  GPa) of the NH<sub>2</sub>-MIL-53(In) framework.<sup>18</sup> A combined computational and experimental work by Yot. *et al.* demonstrated the compliance under mechanical pressure of the related material MIL-47, a vanadium-based MOF with the same topology as MIL-53 and for which adsorption- or temperature-induced breathing has never been observed.<sup>19</sup> In spite of these works, there is still a major lack of experimental data on the fundamental mechanical properties of SPCs, especially when it comes to anisotropy of their elastic behaviour. While full tensorial studies of elasticity are starting to appear on some MOFs, including the measurement of ZIF-8's stiffness tensor by Brillouin scattering,<sup>20</sup> the few experimental studies on mechanical properties of SPCs so far only report the scalar bulk modulus. Indeed, these measurements fail to account for the, *a priori*, tensorial nature of compression and other important elastic properties of SPCs, like their Young's modulus, shear modulus, or Poisson's ratio, have not been experimentally investigated yet.

Only a limited number of solids expand along a specific direction while undergoing total volume reduction under an increase in mechanical pressure. This phenomenon is known as negative linear compressibility (NLC),<sup>21</sup> and has been experimentally observed in some cyanide hybrid materials<sup>22-24</sup> and in a rigid zinc formate framework.<sup>25</sup> These materials

share a common feature, which gives rise to the NLC phenomenon: a wine-rack framework, of the same topology as the framework of the MIL-53 family (see Figure 1).<sup>26</sup>

Indeed, recent quantum chemical calculations have predicted that various MIL-53 materials, as well as other porous SPCs sharing this topology (such as MIL-47 and DMOF-1), should present very large NLC.<sup>27, 28</sup> However, no experimental evidence of NLC on a SPC has been reported so far.

Herein, we report the NLC behaviour of MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al)<sup>29-31</sup> materials confirmed through series of pressure-dependent powder X-ray diffraction experiments performed in a diamond anvil cell (DAC) under different pressurization liquid media.



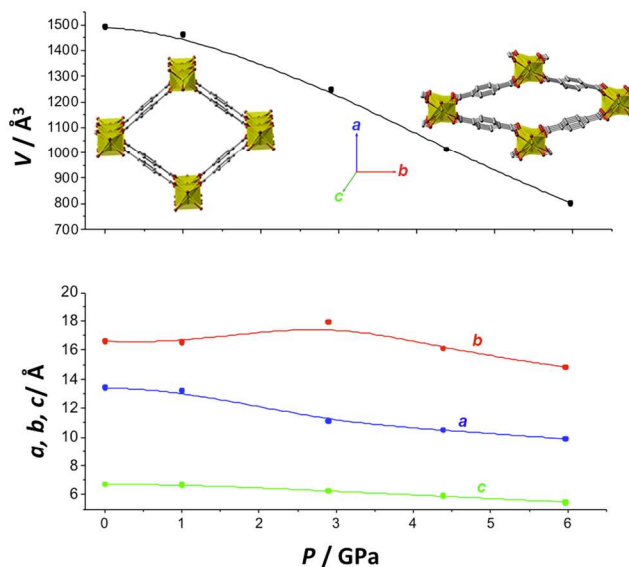
**Figure 1.** (a) The MIL-53 framework in its *lp* configuration, with a wine-rack framework topology and (b) the expected NLC behaviour.

MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al) were synthesized and activated according to literature.<sup>7, 32</sup> The experiments were performed using synchrotron radiation in the beam-line X17C at the National Synchrotron Light Source (NSLS). The DAC consists of two opposing diamonds with the sample chamber created between both culets. In order to avoid axial tensions, a 0.25 mm pre-indented gasket is placed in between the culets and filled with a fluid, used to apply a hydrostatic pressure.<sup>33</sup> The pressure inside the chamber is monitored by observation of the fluorescence of a small ruby chip placed inside the chamber. The position of the fluorescence band of this material has a linear dependence in the region from 0 to 25 GPa.<sup>34</sup> Prior to the insertion into the chamber, the sample was activated and compacted. After that, the chamber was loaded with the pressurization liquid and then pressure was increased step by step. Pressure was measured before and after the experiments and no differences were found.

The X-ray powder diffraction patterns at different pressures were fitted with the simulated patterns calculated on the basis of the published structures.<sup>7, 29</sup> The initial structure models for cell refinements were constructed from unit cell parameters taken from previous reported MIL-53(Al),<sup>7</sup> NH<sub>2</sub>-MIL-53(Al) in *lp* and *np* forms.<sup>29</sup> The resulted pressure-dependent lattice parameters were obtained by Rietveld refinement, performed on the pressure-applied data using WinPLOTR and FULLPROF software.<sup>35, 36</sup> A pseudo-Voigt function was chosen to generate the line shape of the diffraction peaks. First, the zero offset, the scale factor, twelve background terms, profile parameters and the unit cell were refined. The materials were considered amorphous and lead to unreasonable pattern matching when the diffraction peaks became broad and their intensities were less than 5.0% of the

background level, complying 8 FWHM range for calculation of single reflection.

In Figure 2 the changes in volume and cell parameters in MIL-53(Al) are presented as a function of the applied pressure, using mineral oil as pressure-transmitting medium (lattice parameters data of the pressure dependent experiments with mineral oil and ethanol as pressure media in MIL-53 (Al) can be found in Table S1 and Table S2, respectively). Despite the fact that only few data points could be collected, important information can be extracted from these results. In first place, the material is crystalline up to 6 GPa, in the same order of magnitude as the most pressure resistant MOFs.<sup>37</sup>

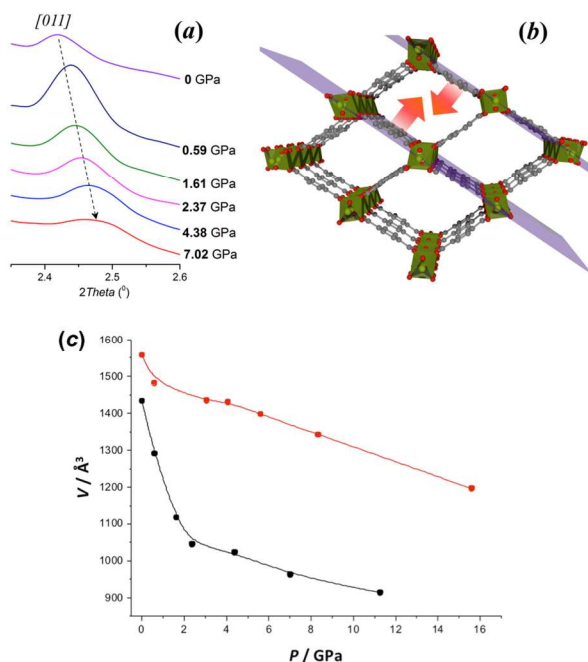


**Figure 2.** Evolution in cell volume (top) and lattice parameters (bottom) of MIL-53(Al) upon increasing hydrostatic pressure using mineral oil as pressurization medium. The lattice parameters are shown in blue (a), red (b) and green (c). Lines are only for guidance.

When focusing on the evolution of the different cell parameters (Table S1), two successive regimes can be observed. First, upon increasing pressure from 0 to 3 GPa, the material expands in the *b* direction while contracting in the *a* and *c* directions, demonstrating NLC in one direction. The linear compressibilities calculated in this range are of  $\beta_a = 23 \text{ TPa}^{-1}$ ,  $\beta_b = -28 \text{ TPa}^{-1}$  and  $\beta_c = 59 \text{ TPa}^{-1}$ . The negative value along the *b* axis is much larger than those measured in other metal-organic frameworks ( $-4.32 \text{ TPa}^{-1}$  for Ag(mim)<sup>26</sup> and  $-1.8 \text{ TPa}^{-1}$  for [NH<sub>4</sub>][Zn(HCOO)<sub>3</sub>]<sup>25</sup>), demonstrating the very large NLC character of MIL-53(Al) in this pressure range. This large value of  $\beta_b$ , obtained on a wide pressure range, is as expected smaller than the value calculated by quantum chemical calculations in the elastic regime, which corresponds to infinitesimal deformations (i.e. the limit of  $P \rightarrow 0$ ). Then, at higher pressure ( $P \geq 3 \text{ GPa}$ ), the overall pressure-induced contraction dominates the behaviour of MIL-53(Al), showing positive linear compressibility along all axes.

Similar experiments performed on the functionalized NH<sub>2</sub>-MIL-53(Al) are shown in Figure 3. The change in cell volume is displayed for the

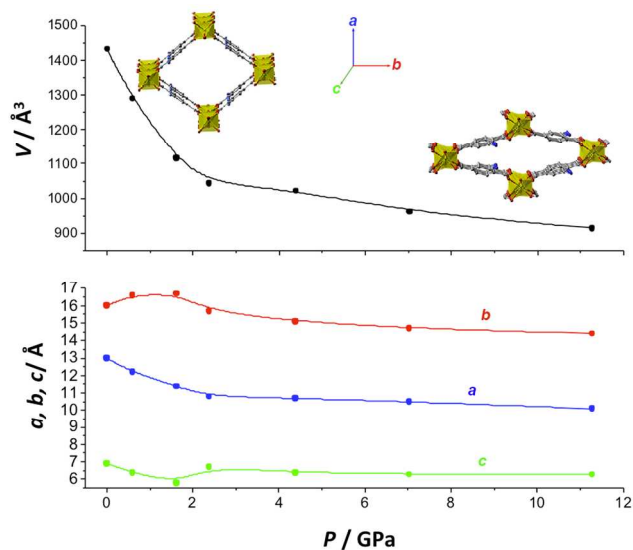
two different pressure media (the lattice parameters for both series of experiments can be found on Table S3 and Table S4 for mineral oil and ethanol as pressure media, respectively). When using mineral oil, two different regions can be observed: (i) from 0 up to 2 GPa and (ii) from 2 to more than 11 GPa, where the material becomes amorphous. In the first region, the cell volume is decreased from 1433 Å<sup>3</sup> to around 1000 Å<sup>3</sup>, matching the change in volume corresponding to the *lp* to *np* transition. The fact that the starting cell volume is 1433 Å<sup>3</sup> indicates that the mineral oil penetrates into the pores (in the absence of adsorbate NH<sub>2</sub>-MIL-53(Al) displays a smaller cell volume), something that could not be concluded in the case of MIL-53(Al).



**Figure 3.** (a) Displacement of peak corresponding to [011] plane as a function of applied pressure on NH<sub>2</sub>-MIL-53(Al) using mineral oil as pressurization medium. (b) The graphical representation of the NH<sub>2</sub>-MIL-53(Al) structure showing the interplanar distance decreasing upon pressurization. (c) Evolution in cell volume upon increasing hydrostatic pressure using ethanol (red) and mineral oil (black). Lines are only for guidance

Results obtained using a smaller fluid such as ethanol are less conclusive, since densely packed ethanol in the pores leads to the formation of a denser phase that does not undergo the well-known *lp* to *np* transition. A clear *lp*-*np* transition is observed upon increasing pressure, attributed to the lower affinity of mineral oil compared with ethanol and to the partial penetration at the starting pressure. With increasing pressure the oil is squeezed out of the sample. Two different bulk moduli were calculated for the two different regions, 7.4 GPa for the pressure range from 0 to 2 GPa and 71 GPa from 2 to 11 GPa. The first value is in line with very soft materials and is in agreement with such a change in volume. In the second region the material behaves like a dense phase, in very good agreement with the bulk modulus obtained using ethanol, 85 GPa, as compressing fluid in the whole pressure range.<sup>9</sup>

Finally, the evolution of the lattice parameters of NH<sub>2</sub>-MIL-53(Al) with pressure was studied using mineral oil as hydrostatic fluid, depicted in Figure 4. As it was the case for MIL-53(Al), the NH<sub>2</sub>-MIL-53(Al) framework shows an expansion in the *b* direction along with a contraction in the *a* direction at pressures up to 2 GPa. These observations are completely consistent with the gradual shifting of the diffraction peak at *ca.* 4.45°, corresponding to the [011] plane, to higher angles (Fig. 3). The values of the linear compressibility in this region are  $\beta_a = 99 \text{ TPa}^{-1}$ ,  $\beta_b = -27 \text{ TPa}^{-1}$  and  $\beta_c = 76 \text{ TPa}^{-1}$ , demonstrating not only anisotropy but also a large degree of NLC as a generic feature of this family of materials. To understand the mechanism that leads to the NLC phenomenon in MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al), the stiff structural inorganic Al(OH) chains can be visualized to act as spindles in the flexible framework that behave as hinges (or centers of flexibility). Dicarboxylate linkers in the orthogonal plane connect these spindles to each other, acting as rigid struts. The rigidity of the struts in this wine-rack geometry enforces a connection between variations in the *a* and *b* lattice parameters: when *a* decreases, *b* increases (in the linear elastic regime, see figure 3b). This gives rise to the NLC phenomenon.



**Figure 4.** Evolution in cell volume (top) and lattice parameters (bottom) of NH<sub>2</sub>-MIL-53(Al) upon increasing hydrostatic pressure using mineral oil as pressurization medium. The lattice parameters are shown in blue (a), red (b) and green (c). Lines are only for guidance

## Conclusions

Refinement of powder X-ray diffraction data collected with a diamond anvil cell and different pressurization media in MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al) show a large pressure resistance and the largest negative linear compressibility of this family of SPCs. This provides experimental confirmation of the Negative Linear Compressibility of these materials, recently predicted on the basis of quantum chemistry calculations. The pressure needed to amorphize these materials was between 5 and 16

GPa for the studied media: ethanol and mineral oil. We attribute the large amorphization resistance to the NLC behaviour of these SPCs, allowing bonds to relax upon pressurization. These results are of the utmost importance not only for the shaping of these MOFs, where the large anisotropy of their mechanical behaviour and NLC might pose some difficulties, but also for matching of the mechanical properties of SPCs with other materials for the processing of composites, e.g. together with polymers for applications as membranes or in optoelectronics.<sup>38, 39</sup>

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### Notes and references

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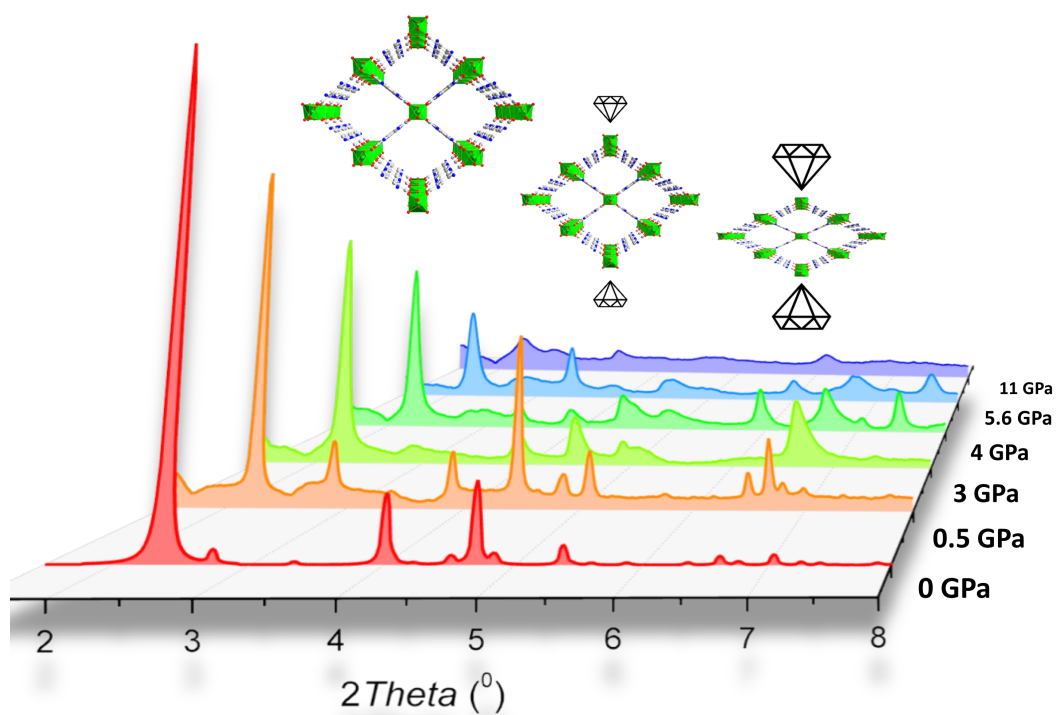
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The Negative Linear Compressibility behaviour of the MIL-53 family of materials is experimentally demonstrated