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Reversible pressure-induced amorphization of a zeolitic imidazolate framework (ZIF-4)[†]Thomas D. Bennett,^a Petra Simoncic,^{bc} Stephen A. Moggach,^d Fabia Gozzo,^b Piero Macchi,^c David A. Keen,^e Jin-Chong Tan^a and Anthony K. Cheetham^{*a}

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We report the reversible pressure-induced amorphization of a zeolitic imidazolate framework (ZIF-4, [Zn(Im)₂]). This occurs irrespective of pore occupancy and takes place *via* a novel high pressure phase (ZIF-4-I) when solvent molecules are present in the pores. A significant reduction in bulk modulus upon framework evacuation is also observed for both ZIF-4 and ZIF-4-I.

Zeolitic Imidazolate Frameworks (ZIFs) are three dimensional structures consisting of rigid MN₄ tetrahedra (M = metal ion), linked through bridging imidazolate (Im) C₃H₃N₂[−] anions. Adopting topologies matching those observed in zeolites and some aluminophosphates,^{1,2} this subfamily of metal–organic frameworks (MOFs) are of primary importance because of their nanoporous properties and thermal stability.³ The high specific gas sorption capacities of some ZIFs has led to proposed application in the fields of gas sorption and separations.^{4,5} Despite this potential, our knowledge of physical properties such as mechanical strength, thermal expansivity and pressure dependant behaviour is underdeveloped.⁶ Studies on more dense, low-porosity materials do exist, such as that on the zeolitic imidazolate framework, ZIF-zni, which displays a cooperative bond rearrangement at 0.8 GPa to a high pressure phase.⁷ Our own single crystal study on the prototypical framework ZIF-8 revealed a guest-driven reversible phase transition at 1.47 GPa.⁸ A synchrotron XRD study demonstrated that, when evacuated, the same ZIF-8 framework undergoes *irreversible* amorphization at 0.34 GPa in a non-penetrating medium, the amorphous framework retaining some porosity.⁹

The thermal amorphization of ZIFs has also been reported, with those containing unsubstituted imidazoles undergoing *irreversible* amorphization to a common phase (termed the *a*-ZIF) at approximately 300 °C, before subsequent recrystallization into the dense ZIF-zni above 400 °C.¹⁰

Curiously, no thermal amorphization of substituted imidazoles (*e.g.* ZIF-8) was observed.¹¹ These frameworks have also been shown to be among the least compliant ZIFs under pressure generated by a diamond indenter tip,^{12,13} bulky substituents such as benzimidazolate conferring rigidity on the framework through projection into the porous cavities.

ZIF-4 crystallizes under ambient conditions in the orthorhombic space group *Pbca* (*a* = 15.402(7) Å, *b* = 15.459(7) Å, *c* = 18.408(8) Å, Vol. = 4383(3) Å³, Fig. 1a) with the *cag* network topology of the mineral variscite. Each unit cell contains 8 nanopores linked by apertures of diameter 2.1 Å, giving a solvent accessible volume (SAV), determined using MERCURY, of 1613.8 Å³, or 36.8% of the unit cell volume

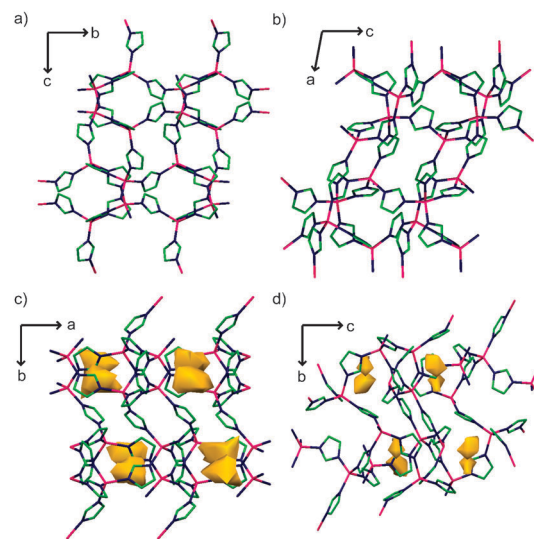


Fig. 1 (a) The unit cell of ZIF-4 viewed down the *a*-axis. (b) The unit cell of ZIF-4-I viewed down an equivalent direction showing the reduction in symmetry. The solvent accessible volume of (c) ZIF-4 as viewed down the *c*-axis and (d) ZIF-4-I along the equivalent axis (yellow isosurfaces). Pink: zinc, green: carbon, blue: nitrogen. Hydrogen atoms omitted for clarity.

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(Fig. 1c). The pores are initially occupied by *N,N*-dimethylformamide (DMF) molecules.

Crystals of ZIF-4 were prepared as reported previously¹⁰ and single-crystal X-ray and powder X-ray diffraction studies used to study the effect of hydrostatic pressure on ZIF-4 (SI-1, SI-2†). A single crystal of dimensions $0.14 \times 0.17 \times 0.22$ mm was selected and loaded into a modified Merrill-Bassett diamond anvil cell (DAC) equipped with 600 μm culet diamonds and a tungsten gasket along with a methanol:ethanol mixture (4:1 ratio by volume), utilized as a small molecule pressure-transmitting fluid (PTF). On increasing pressure to 0.56 GPa the sample underwent a single-crystal to single-crystal, first order phase transition to a previously unobserved phase (termed ZIF-4-I), with the monoclinic space group $P2_1/c$ ($a = 17.759(9)$ Å, $b = 14.457(8)$ Å, $c = 14.829(9)$ Å, $\beta = 100.25^\circ$ Vol = $3741(4)$ Å³, Fig. 1b). Upon undergoing the transition the nanopore volume changes markedly, the SAV decreasing from 34.66% at 0.13 GPa to 22.8% at 0.56 GPa (Fig. 1d). Whilst the high pressure phase transition of ZIF-8 is driven by solvent entering the pores (leading to an initial increase in SAV),⁸ no additional solvent was found to enter the framework in this case, consistent with the marked decrease in pore volume and smaller pore apertures.

Pore volume decreased further with applied pressure until deterioration in diffraction data quality above 3.2 GPa prevented precise structural refinement. Extraction of the unit cell parameters beyond this, however, was possible. Amorphization was observed between 5.01 and 6.5 GPa (Fig. 2). Furthermore, PXRD of a recovered bulk powder sample that had been taken to 8 GPa in a Walker multi-anvil press shows that the amorphization is reversible (Fig. S0).

A second-order Birch–Murnaghan equation of state (EoS) was fitted to the hydrostatic data, yielding a bulk modulus, K_0 , for ZIF-4-I of 16.5(5) GPa (Fig. 2a). Meaningful comparison with ZIF-8 and ZIF-zni ($K_0 = 6.52$ and 14 GPa, respectively) cannot be made because of the presence of solvent within ZIF-4-I. Regrettably, an estimate of K_0 for ZIF-4 could not be obtained from the single crystal study due to the availability of only two data points before the phase transition.

To further investigate this pressure dependant behaviour, *in situ* X-ray diffraction data ($\lambda = 0.729852$ Å) were collected at the Swiss Light Source Materials Science (X04SA) powder diffraction station. Powdered sample was placed in a gas-membrane Boehler-type anvil cell and the pressure was

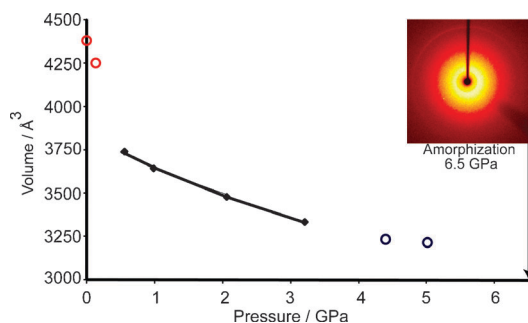


Fig. 2 The evolution of the unit cell volume of ZIF-4 as a function of hydrostatic pressure, complete with equation of state curve fitted to data from the ZIF-4-I phase. Open red circles; ZIF-4, black diamonds; ZIF-4-I. Inset—diffraction pattern at 6.5 GPa.

increased gradually until amorphization was observed. Four distinct loadings were carried out: ZIF-4 with occupied pores with small and large molecule PTFs (measurements A and B, respectively) and evacuated ZIF-4 with small and large molecule PTFs (measurements C and D, respectively). The evacuated samples were prepared by heating a powder ZIF-4 sample to 200 °C under vacuum for 5 h. Le Bail analysis was used to determine the lattice parameters at each pressure. Full experimental details along with initial Rietveld refinement of the structures are available in SI-2.†

Measurement A confirmed the presence of ZIF-4-I at 0.12 GPa and the amorphization by 4.53 GPa. Measurement B used Daphne Oil 7474 (DO), a large molecule PTF. The phase transition to ZIF-4-I was noted between 0.21 and 0.32 GPa, amorphization occurring between 2.61 and 6.43 GPa. From this, it is clear that the nature of the hydrostatic medium does not preclude the phase transition and amorphization of ZIF-4. Significantly, the *in situ* reversible amorphization of ZIF-4 was again found (Fig. 3a). Whilst the properties of the amorphous phase were not investigated, a reversible change in sorption characteristics is implied, based on the porous structure of ZIF-4-I. The recovered crystalline ZIF-4 cell volume was found to have decreased by 0.07%, compared to the starting material at the same pressure (Table S3†).

Both samples of evacuated ZIF-4 (measurements C and D) displayed the same reversible amorphization, albeit with excessive peak broadening upon returning to ambient pressure (Fig. 3b).

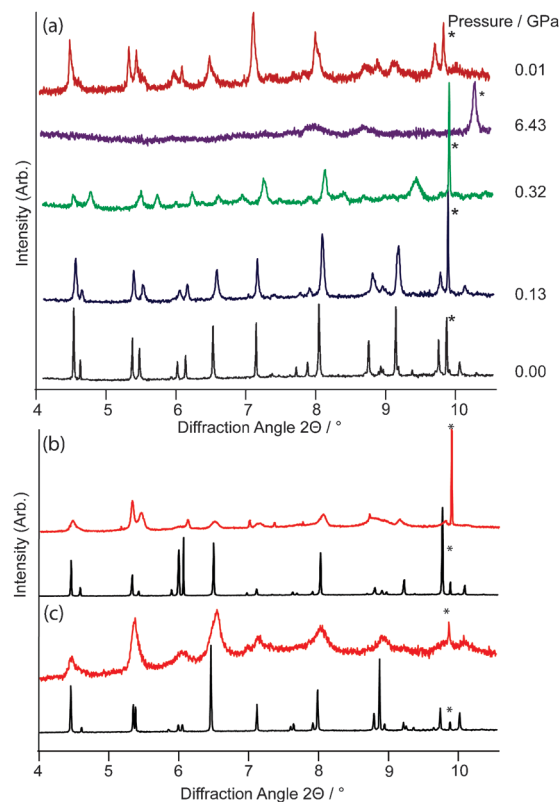


Fig. 3 (a) Diffraction data for measurement B, ZIF-4 (solvent containing) in DO, with increasing pressure. (b) Measurement D, ZIF-4 (solvent free) in DO (c) measurement C, ZIF-4 (solvent free) in methanol:ethanol. Black traces indicate ambient pressure, red indicates return to ambient pressure. SiO₂ standard peaks indicated by *.

Table 1 Summary of the pressure dependant behaviour of ZIF-4 in the five experimental series, the phase transition referring to the transition from ZIF-4 to ZIF-4-I

Exp.	Solvent occupied	PTF	Phase transition	Amorphization	K_0 ZIF-4	K_0 ZIF-4-I
Single crystal	Yes ^a	MEV(small)	0.13–0.56	5.01–6.48		16.5(5)
A	Yes	MEV(small)	0.00–0.12	2.02–4.53		
B	Yes	DO (large)	0.21–0.32	2.61–6.43	7.7(8)	15(2)
C	No	MEV(small)	N/A	1.49–4.54		
D	No	DO(large)	N/A	0.35–0.98	2.6(1)	

However, ZIF-4-I was not observed, suggesting that its formation may be induced by the rearrangement of DMF molecules within the framework.

Penetration of the small molecule PTF into the framework was evidenced by a separate experiment whereby the unit cell parameters of evacuated ZIF-4 before and after soaking in the small molecule PTF were elucidated. The cell volume showed an expansion of 1.88% in the latter, suggesting the larger surface/volume ratio of the powder sample favours sorption. The unit cell volumes of two evacuated single crystal samples of ZIF-4 in a DAC at ambient conditions, in small and large molecule PTFs, were determined in order to check the difference between single crystal and powder samples. The unit cell volumes were similar to one another, but distinct from measurements C and D, confirming that the small molecule PTF does not readily enter the pore system of a single crystal sample of ZIF-4.

The evacuated sample amorphized between 0.35 and 0.98 GPa using DO, compared to 1.49–4.54 GPa when using the methanol : ethanol mixture. The former pressure range can also be compared to that in measurement B (2.61–6.43 GPa), yielding the result that occupation of the framework by DMF molecules plays a critical role in its pressure-dependant stability. This is particularly striking, given that our previous work on the response of evacuated and filled ZIF-8 to indentation pressure revealed Young's modulus differences of less than 5%.¹²

The slightly larger stability range of ZIF-4 in DO (measurements B and D) allowed the fitting of the changes in lattice volume to a second-order Birch–Murnaghan EoS. Bulk moduli show a large decrease from $K_0 = 7.7(8)$ to $K_0 = 2.6(1)$ upon evacuation of the framework. A bulk modulus of $K_0 = 15(2)$ GPa was found for ZIF-4-I from measurement B, consistent with the single crystal study. A summary of the pressure dependant behaviour of all four samples is given in Table 1 and EoS fits are shown in Fig. S3.†

In conclusion, a reversible pressure-induced amorphization of a ZIF has been reported for the first time. It should be expected that other unsubstituted ZIFs (e.g. ZIF-1, -2, -3 and -10) will undergo similar reversible amorphization. We observed that the mechanical stability under hydrostatic loading can decrease significantly upon framework evacuation, an outcome that is critical for technical applications. The pressure at which amorphization occurs is lower when a large molecule PTF is used. A difference in behaviour between single crystal and powder samples is found, with framework penetration by a

small molecule PTF in a powder sample. The absence of a transition to the dense ZIF-zni (in the case of evacuated ZIF-4) in the pressure range investigated suggests that the amorphization process occurs with retention of the metal tetrahedra and associated structural connectivity. This is in marked contrast to the irreversible *thermally* induced transitions reported for ZIFs,^{10,11} and zeolites,¹⁴ in which the medium range structural connectivity is altered. The pressure amorphized ZIF is therefore unlikely to adopt the same Continuous Random Network topology as those which have been thermally amorphized; this is also the case with zeolites.¹⁵

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