

Anisotropic mechanical properties of polymorphic hybrid inorganic–organic framework materials with different dimensionalities

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Abstract

Hybrid inorganic–organic framework materials have recently developed into an important new class of solid-state materials. Their mechanical properties are as yet unexplored, although they could be of great utility in view of their enormous structural and chemical diversity. The anisotropic mechanical properties of two new copper phosphonoacetate polymorphs, one a three-dimensional coordination polymer and the other a layered material with inter-layer hydrogen bonding, have been studied by nanoindentation with single crystals. The elastic and plastic anisotropy, the onset of plasticity and the fracture toughness anisotropy have been investigated along the main crystallographic directions. The anisotropy of the mechanical properties can be correlated directly with the underlying crystalline structures. For example, the elastic modulus is largest (up to ~ 90 GPa) along directions that are dominated by inorganic chains or sheets and smallest (~ 35 GPa) along directions where the organic ligands provide the primary linkages. This study also highlights the capabilities and limitations of nanoindentation for studying the anisotropic mechanical properties of hybrid framework materials.

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1. Introduction

Hybrid inorganic–organic framework materials are single-phase crystalline compounds containing both inorganic and organic moieties that coexist as integral parts of a network with infinite bonding connectivity in at least one dimension [1]. This new class of material exhibits enormous chemical and structural diversity, which ranges from one-dimensional (1D) chains to 2D sheets and to 3D frameworks, and may include both organic and inorganic connectivities. Here, it is important to emphasize that hybrid framework materials are not hybrid composites, in which the organic and inorganic components are present as separate and distinct phases. Hybrid framework materials also exclude molecular or oligomeric systems (e.g. supramolecular assemblies) that form networks via non-covalent bonding, and systems in which the organic component appears

only as a guest within an inorganic cavity (e.g. in classical zeolites).

Interest in the field of hybrid inorganic–organic framework materials has seen enormous growth in the past decade, because they offer huge opportunities for creating exciting properties or unique combinations of properties that have the potential to be of great technological importance. Most of the hybrid framework materials known to date can be classified into two categories [1]. (i) Coordination polymers are composed of isolated metal (M) atoms or clusters that are connected by multifunctional organic ligands (L) to form extended arrays via M–L–M connectivity. Nanoporous coordination polymers, commonly known as metal–organic frameworks (MOFs), are of interest for potential applications in catalysis, sensors, gas separation and storage [2–5]. (ii) Extended inorganic hybrids are dense hybrid frameworks that are more similar to classical inorganic materials and are based upon infinite metal–anion–metal, e.g. metal–oxygen–metal (M–O–M) connectivity. The development of dense hybrid frameworks has important

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ramifications for a wide range of functional device materials, particularly in relation to their electronic, magnetic, optical and multiferroic properties [6–9].

Although the pace of research in the hybrid materials area has accelerated dramatically and a large number of groups worldwide are now active in this field, one of the areas that has not yet been explored concerns their mechanical properties. In view of the vast chemical and structural diversity of hybrids, their mechanical properties have the potential to show a richness of behaviour that cannot be obtained in purely inorganic or organic systems. There is also arguably unlimited scope for tuning the mechanical properties by variation of the organic and/or inorganic building blocks. This is an area that deserves more attention since, for almost all viable applications, knowledge of mechanical properties is essential for designing devices with optimal performance so as to survive both static and cyclic loadings, sometimes coupled with substantial thermal stresses. The lack of progress in this area may, in part, be due to the difficulty in preparing good quality single crystals of hybrid framework materials needed for mechanical studies, but also because of the limitations imposed by existing mechanical testing techniques. Work to date has dealt only with the mechanical properties of nanoporous MOF-5 (i.e. $\text{ZnO}_4(1,4\text{-benzenedicarboxylate})_3$). Bahr et al. [10] recently measured the Young's modulus of cubic MOF-5 via nanoindentation, and found its value (2.7 ± 1.0 GPa) to be about an order of magnitude lower than density functional theory predictions [11,12]. They attributed this discrepancy to surface roughness effects and sensitivity of MOF-5 towards atmospheric conditions. To the best of our knowledge, the mechanical behaviour of dense hybrid frameworks has never been reported before, despite their potential to offer many key physical properties such as ferromagnetism, photoluminescence, metallic- and semi-conductivity [6]. Moreover, because of their architectures, dense hybrids are expected to be mechanically more robust compared with the majority of porous hybrid systems.

Nanoindentation has become a widely adopted technique for characterizing the mechanical properties of materials at small length scales, especially that of bulk isotropic materials [13]. There have also been increasingly more reports on the use of nanoindentation to probe the mechanical properties of anisotropic materials, such as single crystals [14–18] and heterogeneous materials with hierarchical structures (e.g. bones) [19,20]. However, due to the presence of anisotropy, the analysis of indentation response is less straightforward and requires further assumptions to be made. Therefore, care is needed when interpreting the modulus and hardness values extracted from anisotropic systems, since these may well not be their intrinsic properties, but can depend upon factors such as tip geometry, elastic and plastic responses, and sample boundary conditions [21].

In the present work, we have studied two low-symmetry polymorphs of copper phosphonates using nanoindentation. The availability of good quality single crystals of the polymorphs provided us with an interesting oppor-

tunity to compare the mechanical properties of two anisotropic hybrid frameworks that differ only in terms of their crystal structures. Our findings reveal the diverse range of elastic and plastic responses that can be found in hybrid materials, and enable us to establish relationships between mechanical properties and the corresponding crystalline structures.

2. Experimental methods

2.1. Materials synthesis and structure characterization

Synthesis of polymorph 1, $\text{Cu}_{1.5}(\text{H}_2\text{O})(\text{O}_3\text{PCH}_2\text{CO}_2)$: a mixture of CuO (1 mmol) (supplied by Aldrich Chemical Co.) and phosphonoacetic acid (1 mmol) (Aldrich) in 5 ml of deionized water was placed in the polytetrafluoroethylene liner of a 23 ml autoclave and stirred for 10 min. The liner was then placed in the autoclave, sealed and heated at 180 °C for 10 days (initial and final pH: 3.0, 2.0). The final product, consisting of blue prismatic crystals (Fig. 1a), was washed with water and dried at 60 °C.

Synthesis of polymorph 2, $\text{Cu}_{1.5}(\text{H}_2\text{O})(\text{O}_3\text{PCH}_2\text{CO}_2)$: the same synthesis procedure as polymorph 1 was used, but with 12 ml of deionized water and heating for 2 days (initial and final pH: 1.0, 2.5). The product consisted of green rectangular platey crystals which are polymorph 2 (Fig. 1f), and powder and crystals of polymorph 1.

The crystal structures of the polymorphs (Table 1) were determined by single-crystal X-ray diffraction, performed on a Bruker SMARTCCD diffractometer equipped with a normal-focus 2.4 kW sealed tube X-ray source (Mo K_α radiation, $\lambda = 0.71073$ Å), operating at 50 kV and 40 mA. In each case, a hemisphere of intensity data was collected at room temperature. A multi-scan correction on the basis of symmetry-equivalent reflections was applied using the SADABS program [22] and the structures were solved by direct methods using the SHELXTL package of programs [23]. The hydrogen atoms were found in the Fourier difference maps.

2.2. Mechanical properties characterization

Nanoindentation was performed at ambient temperature using an MTS NanoIndenter[®] XP (MTS Corp., Eden Prairie, MN), equipped with a continuous stiffness measurement (CSM) module. The instrument was placed within an isolation cabinet that shielded against thermal instability and acoustic interference. Two types of diamond indenter tips were used: (i) a three-sided pyramidal Berkovich indenter with a sharp tip (end radius ~ 50 nm) was used to measure indentation modulus (M) and hardness (H), and to induce cracks for estimating fracture toughness; and (ii) a spherical tipped indenter (nominal radius, $R = 10$ μm) was employed to study the elastic–plastic transition and to investigate the effects of tip geometry on fracture behaviour. Calibration was performed using a fused silica standard, with elastic modulus ($E = 72$ GPa) and hardness ($H = 9$ GPa) that are

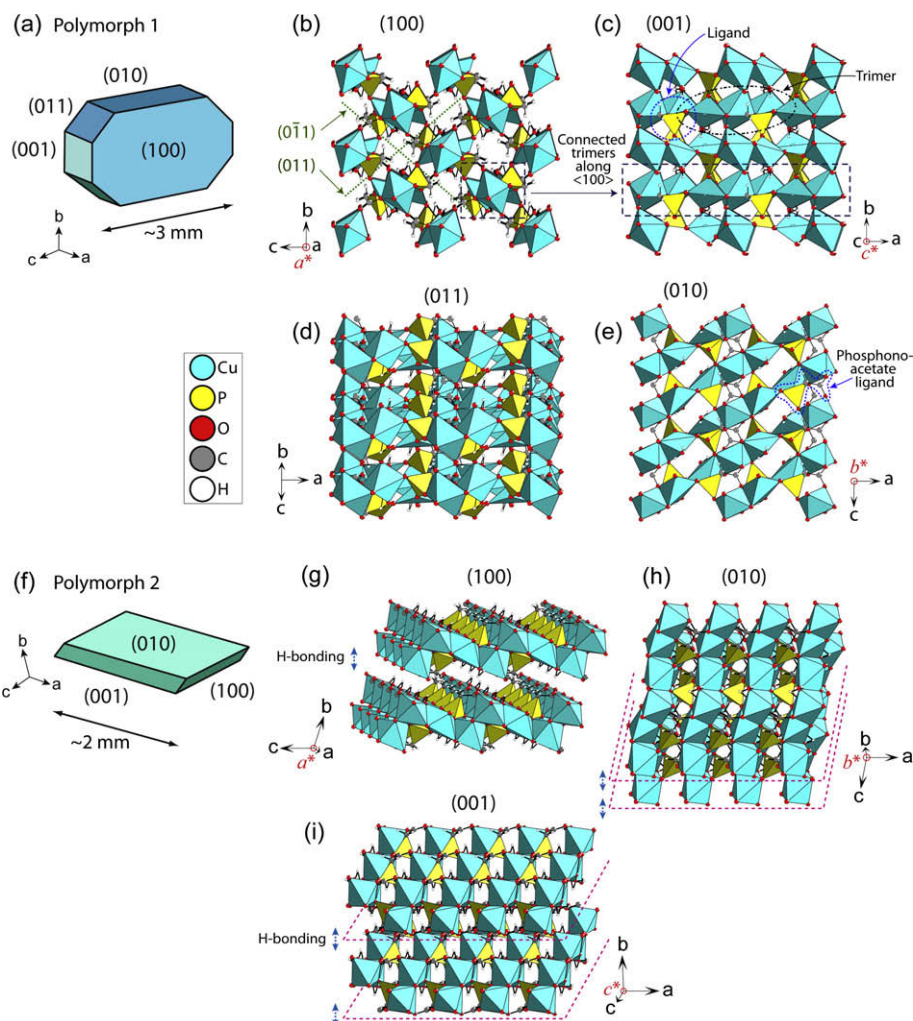


Fig. 1. Crystalline structures of polymorphs 1 (monoclinic) and 2 (triclinic). (a) Single-crystal morphology of polymorph 1 and its low index faces. (b–e) Views of polymorph 1 perpendicular to the (1 0 0), (0 0 1), (0 1 1) and (0 1 0) planes, respectively, which are normal to the nanoindenter axes. (f) Single-crystal morphology of polymorph 2 and its low index faces. (g–i) Views of polymorph 2 perpendicular to the (1 0 0), (0 1 0) and (0 0 1) planes, respectively. (g) 2D layer spacing viewed along the a^* -axis direction, i.e. normal to the (1 0 0) plane and approximately parallel to the layers. The blue dotted arrows designate inter-layer hydrogen bonds. (h) Plan view of two individual layers as viewed along the b^* -axis direction, i.e. normal to (0 1 0) plane and almost perpendicular to the layers. (i) The layers are inclined at oblique angles when viewed along the c^* -axis direction, i.e. normal to (0 0 1) plane. Note that the red dotted lines highlight the layers.

Table 1
Summary of the crystal structure data for polymorphs 1 and 2.

	Polymorph 1	Polymorph 2
Formula	$\text{Cu}_{1.5}(\text{H}_2\text{O})[\text{O}_3\text{PCH}_2\text{CO}_2]$	$\text{Cu}_{1.5}(\text{H}_2\text{O})[\text{O}_3\text{PCH}_2\text{CO}_2]$
Formula weight	250.33	250.33
Space group	P 2 ₁ /c	P-1
Unit cell parameters	$a = 8.2631(17)$ $\alpha = 90$ $b = 7.6451(15)$ $\beta = 90.52(3)$ a, b, c (Å); $c = 8.9708(18)$ $\gamma = 90$	$a = 4.6712(9)$ $\alpha = 108.18(3)$ $b = 8.0026(16)$ $\beta = 100.68(3)$ $c = 8.1100(16)$ $\gamma = 92.36(3)$
Unit cell volume (Å ³)	566.7(2)	281.44(10)
Density (g cm ⁻³)	2.934	2.954

The complete dataset can be obtained from Ref. [58].

of the same order of magnitude as the polymorphic hybrid crystals being investigated here. Thermal drifts were ensured to be consistently low (typically $<0.05 \text{ nm s}^{-1}$). To avoid interaction of deformed zones, the inter-indent spacing was ensured to be at least 50 times the indentation depth. The shape of the residual indents were characterized using a Veeco Dimension V atomic force microscope (AFM), under tapping mode to map the 3D morphology of the indent after complete unloading and also to quantify the extent of material pile-up.

Untwinned single crystals were used in our nanoindentation studies. The indices of the crystal faces as depicted in Fig. 1a and f were identified via single-crystal X-ray diffraction. The surfaces of as-synthesized crystals can be uneven due to growth steps and dissolution pits, with heights and/or depths ranging from tens of nanometers to several

microns. Surface features with roughness amplitude larger than that of the contact dimension (end radius of sharp tip) can impair surface contact detection and result in inaccurate contact area determination. To overcome these difficulties, individual crystals were cold-mounted using the Epofix resin (Struers Ltd.) and then polished using increasingly fine diamond suspensions, followed by a final polishing step using 0.05 μm colloidal silica suspension. The final (rms) surface roughness was found to be of less than 10 nm, as determined from AFM topographic images. The mounted and polished crystal surfaces were oriented to within $\sim 0.1^\circ$ of the desired orientation (i.e. normal to the indenter axis). A limited number of tests were also conducted on (apparently) flat regions of as-synthesized crystals, directly bonded onto a metallic sample holder using cyanoacrylate adhesives. Similar moduli and hardnesses were obtained (but with larger data scatter due to roughness effects), hence confirming that cold-mounting and careful polishing operations did not induce noticeable damages. Consequently, all results presented here were collected from polished samples since they offer higher quality surfaces and also facilitate probing of narrow surfaces (e.g. the (1 0 0) facet of polymorph 2; see Fig. 1f).

Nanoindentation experiments were conducted using two different techniques: (i) quasi-static (load-controlled) mode and (ii) dynamic displacement-controlled CSM mode. They differ in the way in which the elastic contact stiffness (S) is obtained. Under the quasi-static mode, S is determined from the slope of the load–displacement (P – h) curve at the initial point of unload (i.e. $S = dP/dh$), therefore M and H can be found only at the maximum indentation depth. In contrast, under the CSM mode, M and H can be obtained as a function of indentation depth by continuously monitoring the change in S . This was achieved by superimposing a 2 nm sinusoidal displacement at 45 Hz onto the primary loading signal, while analysing the system response via a frequency-specific amplifier [13]. The loading and unloading strain rates were set at $5 \times 10^{-2} \text{ s}^{-1}$. At the preset displacement (500 nm), the indenter was held for 30 s prior to unloading (to minimize creep effects). The elastic contact stiffness determined from the P – h curves is later used to calculate the reduced modulus (E_r), by [24]:

$$E_r = \frac{\sqrt{\pi}}{2\beta} \frac{S}{\sqrt{A_c}} \quad (1)$$

where A_c is the contact area under load (based on the calibrated tip areal function) and β is a constant that depends on the geometry of the indenter ($\beta = 1.034$ for a Berkovich tip and $\beta = 1$ for a spherical tip). The method proposed by Oliver and Pharr (O&P) [24] to extract the sample elastic modulus from the reduced modulus assumes isotropic elastic properties, which is normally not the case for single crystals. To account for the effects of anisotropy in single crystals, it has been shown [14,16,25] that the modulus obtained from nanoindentation of a single crystal is more

appropriately represented as an “indentation modulus”, given by:

$$\frac{1}{E_r} = \frac{1}{M_{hkl}} + \left(\frac{1 - \nu_i^2}{E_i} \right) \quad (2)$$

where M_{hkl} is the indentation modulus of an (hkl) plane, and E_i and ν_i are the elastic modulus and Poisson's ratio of the indenter, respectively (for diamond: $E_i = 1141 \text{ GPa}$ and $\nu_i = 0.07$). Here, M_{hkl} is in fact a complicated function of the single-crystal elastic constants which cannot be expressed in a closed-form, but further simplifications are possible for the case of high-symmetry cubic crystals [14]. However, for the case of low-symmetry crystals (and other heterogeneous materials), rather than obtaining absolute (intrinsic) values, the indentation modulus can be used for comparing the relative stiffnesses.

The indentation hardness based on the O&P method, H , is determined by dividing the applied load (P) by the contact area developed under that load (A_c):

$$H = \frac{P}{A_c} \quad (3)$$

A_c is calculated from the contact depth (h_c), which is modelled as the contact between a paraboloid of revolution with an isotropic elastic half-space, given by [24]:

$$h_c = h_{\max} - 0.75 \left(\frac{P}{S} \right) \quad (4)$$

where $h_{\max}$ is the maximum indentation depth and $0.75(P/S)$ denotes the extent of elastic recovery (h_e). Herein, indentation modulus and indentation hardness are simply referred to as “modulus” and “hardness”, respectively.

3. Results and discussion

3.1. Synthetic and structural findings

While a growing number of metal phosphonoacetate frameworks are known [26–32], the copper-based materials have not been widely studied. $\text{Cu}_3(\text{H}_2\text{O})_2[\text{O}_3\text{PCH}_2\text{CO}_2]_2$, polymorph 1, is a new phosphonoacetate coordination polymer (Fig. 1a–e). It contains distorted CuO_6 octahedra and distorted $\text{Cu}(\text{H}_2\text{O})\text{O}_4$ trigonal bipyramids in which the planar oxygens of the CuO_6 octahedra are shared with the trigonal bipyramidal CuO_5 units to form $\text{Cu}_3(\text{H}_2\text{O})_2\text{O}_{10}$ trimers (Fig. 1c). Successive trimers are linked by two phosphonate units to form chains in the [1 0 0] direction, and the chains are cross-linked by further phosphonate and carboxylate connections to form a dense 3D framework. The (0 1 1) and (0 $\bar{1}$ 1) planes, which can be drawn through the organic cross-links between the chains, have low bond density and no metal–oxygen bonds (green dotted lines in Fig. 1b).

$\text{Cu}_3(\text{H}_2\text{O})_2[\text{O}_3\text{PCH}_2\text{CO}_2]_2$, polymorph 2, is a new layered framework (Fig. 1f–i). It resembles a known $\text{Co}_3(\text{O}-$

H)(O₃PCH₂CO₂)₂[H₃O]₂, which has the same layer construction but with different layer registry and contains water between the layers [33]. There are two Cu²⁺ sites, both distorted Cu(H₂O)O₅ octahedra, which are edge-sharing and form jagged chains in the *c*-direction (see Fig. 1g and h) with 1D metal–oxygen–metal (Cu–O–Cu) connectivity. The chains are linked by phosphonoacetate groups to form 2D layers which are hydrogen-bonded to each other. The layers are approximately parallel to the (0 1 0) plane, nearly perpendicular to the (1 0 0) plane, and oblique to the (0 0 1) plane (Fig. 1g–i). The results of time-dependent reactions indicate that polymorph 1 is probably more stable than polymorph 2, which is consistent with the higher dimensionality of the former (although its density is slightly lower). However, the difference in energy must be very small because it can take up to 10 days to form the more stable polymorph.

3.2. Anisotropy of mechanical properties

The fact that polymorphs 1 and 2 are three-dimensional and layered framework structures, respectively, enabled us to probe the relationships between the crystal structures and the anisotropies of the mechanical properties. In this study, nanoindentation experiments using sharp and spherical tipped indenters were performed on single crystal faces to characterize a range of mechanical properties, including indentation modulus, hardness, incipient plasticity, creep and fracture behaviour. Each of these properties is discussed in turn below.

3.2.1. Elastic anisotropy

The typical *P*–*h* curves of polymorphs 1 and 2 obtained with the Berkovich tip under the CSM mode, are depicted in Fig. 2a and b, respectively. For each polymorph, it can

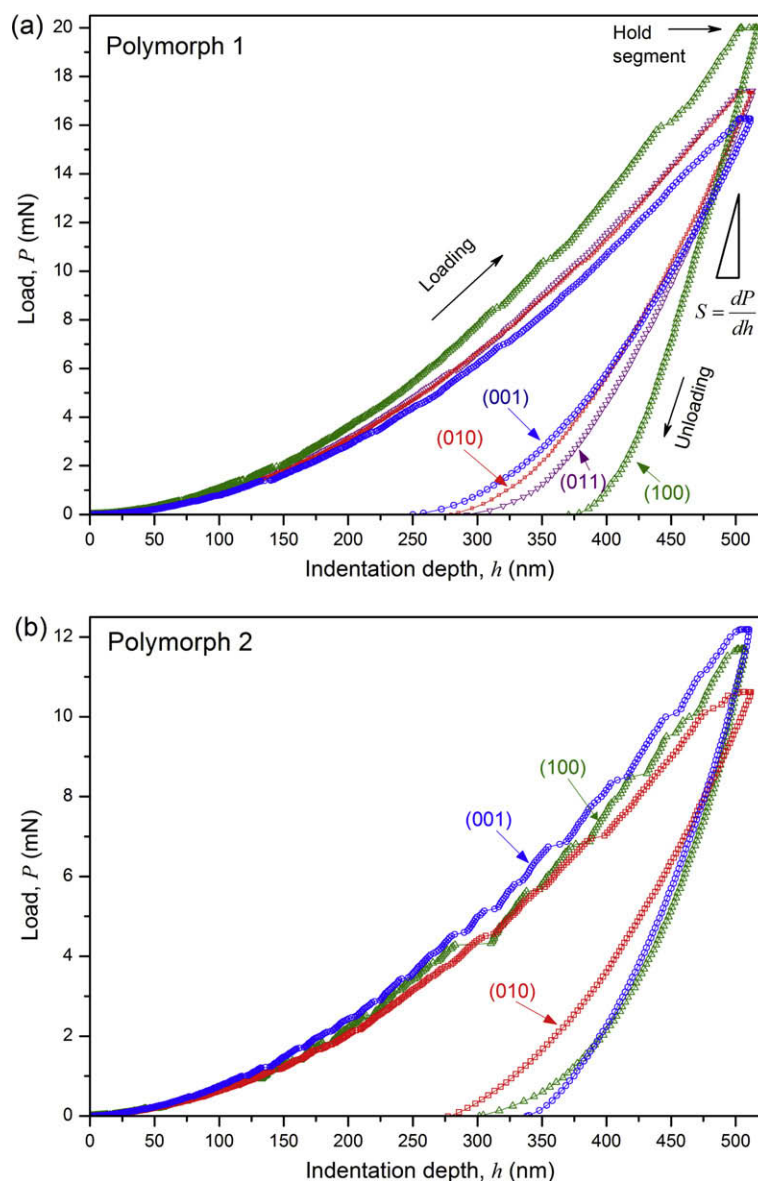


Fig. 2. Typical *P*–*h* curves of (a) polymorph 1 and (b) polymorph 2 along the main crystallographic orientations. All tests were performed using the CSM mode with a Berkovich nanoindenter up to penetration depths of ~500 nm.

be seen that the slope of the unloading segment (i.e. measure of elastic contact stiffness) is unique to each crystal facet, which indicates elastic anisotropy. Moreover, although the maximum penetration depths were the same for all faces ($h_{\max} \sim 500$ nm), the extent of elastic recovery was significantly different. The indentation moduli of the crystal faces as a function of indentation depths for polymorphs 1 and 2 are shown in Fig. 3a and b, respectively. The larger scatter in the moduli data within the first 50 nm can be ascribed to surface roughness and indenter tip imperfection. Therefore, the mean values were determined at depths from 100 to 500 nm (Table 2), where the indentation moduli remained relatively constant. The moduli of the specific crystal faces appeared to be markedly anisotropic, signifying a strong correlation

between stiffness and the underlying crystalline structure. For comparison, indentation moduli obtained from quasi-static tests with single unload at ~ 490 nm were also plotted in Fig. 3a and b. In polymorph 1, the quasi-static results are consistent with the CSM data, but in polymorph 2 they are $\sim 5\%$ lower for both (1 0 0)- and (0 0 1)-oriented faces due to crack developments along the cleavage planes (see Section 3.2.5).

For polymorph 1 (Fig. 3a), the average moduli on the (1 0 0)-, (0 1 0)-, (0 0 1)- and (0 1 1)-oriented faces are (in GPa) 92.7 ± 1.2 , 54.2 ± 0.8 , 49.8 ± 0.7 and 57.3 ± 0.5 , respectively, and the ratio of moduli is M_1 (1 0 0):(0 1 0):(0 0 1):(0 1 1) = 1.86:1.09:1.00:1.15. The maximum change in modulus is $\sim 86\%$ and the (1 0 0) plane is clearly the stiff-

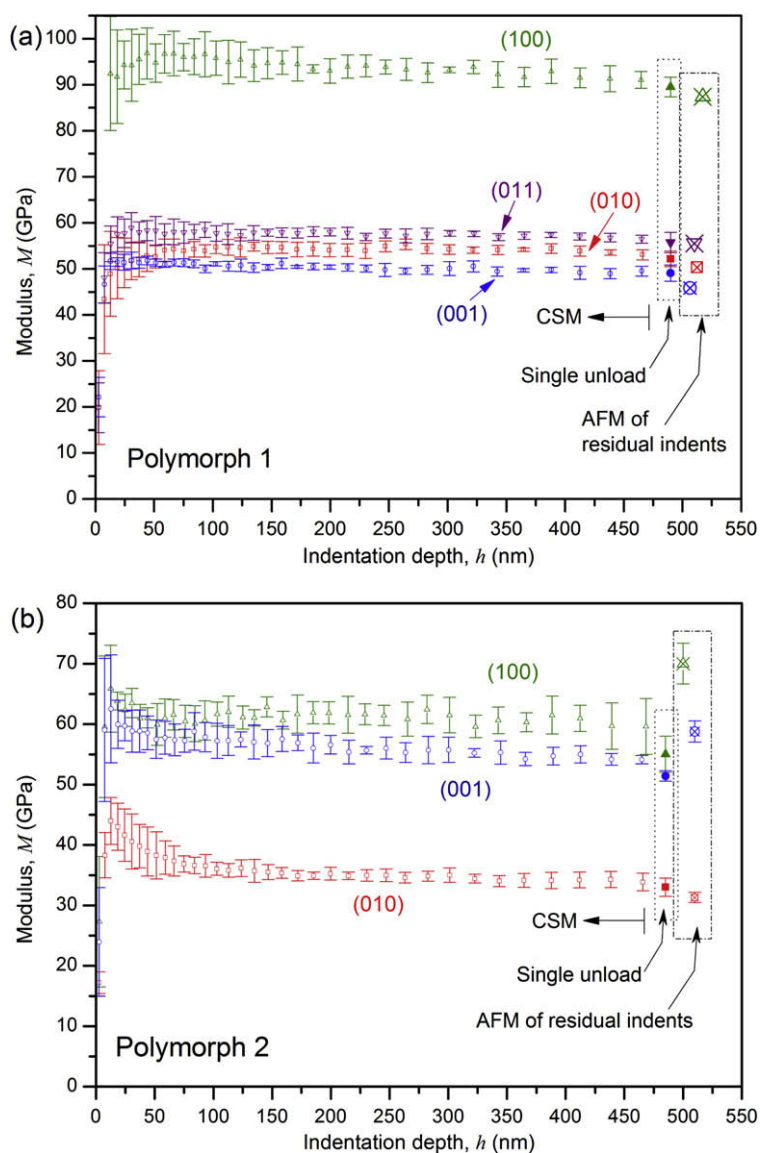


Fig. 3. Indentation moduli along the main crystallographic orientations of (a) polymorph 1 and (b) polymorph 2. The data collected from three different methods with a Berkovich indenter are represented by different symbols: open symbols up to ~ 480 nm are CSM data as a function of indentation depth, filled symbols at ~ 490 nm correspond to single unloading tests, and crossed symbols denote pile-up-corrected moduli determined from AFM of the residual indents. The error bars of CSM and single unloading experiments represent the standard deviation of at least 15 measurements, while they correspond to five measurements for the AFM data.

Table 2

Anisotropies of the mechanical properties of polymorphic copper phosphonoacetate single crystals, measured with a Berkovich nanoindenter.

Mechanical properties	Polymorph 1				Polymorph 2		
	(1 0 0)	(0 1 0)	(0 0 1)	(0 1 1)	(1 0 0)	(0 1 0)	(0 0 1)
Indentation modulus, M (GPa)	92.7 ±1.2	54.2 ±0.8	49.8 ±0.7	57.3 ±0.5	61.2 ±2.2	34.5 ±0.9	55.2 ±1.1
Hardness, H (GPa)	4.46 ±0.12	4.67 ±0.21	4.49 ±0.10	4.22 ±0.11	2.26 ±0.08	2.52 ±0.11	2.34 ±0.10
Fracture toughness, K_{IC} (MPa m ^{1/2})	0.284 ±0.046	0.120 ±0.022	0.153 ±0.036	0.184 ±0.029	0.102 ^a ±0.022	0.104 ±0.011	0.107 ^b ±0.016

The moduli and hardnesses are mean values of continuous stiffness measurement (CSM) data, calculated from indentation depths of 100–500 nm (Figs. 3 and 4). The fracture toughness values were found by employing Eq. (8). All errors correspond to standard deviations on at least 15 measurements.

^a Cracks propagated along (0 0 1) only (see Fig. 10g).

^b Cracks propagated along (1 0 0) only (see Fig. 10f).

fest. As illustrated in Fig. 1b, c and e, the phosphonate headgroups link the $\text{Cu}_3(\text{H}_2\text{O})_2\text{O}_{10}$ trimers to form an unbroken chain of Cu–O–Cu–O–Cu–O–P–O–Cu linkages along the a -axis. The cross-linking of trimers by adjacent ligands forms a stiff “backbone structure” oriented along the (1 0 0) direction. Such construction adds additional rigidity to the entire framework, but also gives rise to elastic anisotropy. When indenting the (1 0 0) plane, it can be seen from Fig. 1b that the indenter axis (down the a^* -axis) almost coincides with (1 0 0), where the greatest stiffness was measured. In contrast, the (0 0 1) and (0 1 0) faces have relatively low moduli. Both planes are bound to be more compliant when probed along the c^* - and b^* -axis orientations (Fig. 1c and e), since the (1 0 0) backbone structures are effectively oriented normal to the indenter axis, rendering them less stiff. However, the moduli of (0 1 0) are consistently higher than (0 0 1) throughout the entire depth, probably due to the fact that the former has closer-packed planes, as indicated by the ratio of their interplanar spacings: $d_{(010)}/d_{(001)} \approx 0.85$. Of course, other factors, such as spatial arrangement, orientation and rigidity of phosphonate tetrahedra and carboxylate groups, may also be important (but molecular modelling techniques will be needed to predict such effects; see e.g. [34]). It is also interesting to note that, although the modulus of (0 1 1) falls somewhere between that of the (0 1 0) and (1 0 0) planes, the modulus of (0 1 1) is only ~ 3 GPa greater than (0 1 0). In comparison with (1 0 0), the modulus of (0 1 1) appears to be significantly lower, by ~ 35 GPa, presumably because the stiff chains of interconnected trimers along (1 0 0) are effectively oriented normal to the loading direction (see Fig. 1d).

Our findings on polymorph 1 demonstrate that, despite the complex 3D stress field that developed under the Berkovich indenter, the indentation moduli of the different crystal facets are clearly distinguishable. Of course, due to the averaging of anisotropic elastic constants found along the indentation direction, the measured moduli will deviate from the intrinsic values. This may also explain the small anisotropy found between the (0 0 1), (0 1 0) and (0 1 1) facets, which differ from each other by only $\sim 10\%$ (their intrinsic values can only be determined if the

full set of elastic constants are known). However, for low-symmetry single crystals (polymorph 1 is monoclinic), the measured moduli will be biased towards the intrinsic modulus along the indenter axis. Hay et al. [35] have shown that, for β -silicon nitride (hexagonal) single crystals, the modulus obtained from nanoindentation is strongly dependent upon the elastic properties along the indentation direction but only weakly affected by the transverse directions. This seems to be the case for the (1 0 0) facet of polymorph 1, in which chains of interconnected trimers are oriented along the (1 0 0) indenter axis.

For polymorph 2 (Fig. 3b), the average moduli of the (1 0 0)-, (0 1 0)- and (0 0 1)-oriented faces are (in GPa) 61.2 ± 2.2 , 34.5 ± 0.9 and 55.2 ± 1.1 , respectively, and the ratio between the three planes is M_2 (1 0 0):(0 1 0):(0 0 1) = 1.77:1.00:1.60, giving a maximum change in modulus of $\sim 77\%$. Primarily due to its layered nature, a high degree of elastic anisotropy is expected. The (1 0 0) and (0 0 1) facets were found to be of significantly higher moduli, but with larger experimental uncertainty due to the extensive pop-in events (displacement bursts in Fig. 2b). The (0 1 0)-oriented face (Fig. 1h) was found to have the lowest modulus, indicating that 2D layers which are hydrogen-bonded together are relatively compliant when loaded along the normal orientation (b^* -axis). The strength of chemical interaction for hydrogen bonding is typically of ~ 5 – 65 kJ mol^{−1}, which is relatively lower than covalent (~ 350 kJ mol^{−1}) and most coordination bonding (50 – 200 kJ mol^{−1}) [36]. It follows that the inter-layer hydrogen bonds are relatively weak and exhibit lower resistance against external compressive (and shear) stresses. By contrast, the (1 0 0)-oriented face (Fig. 1g) exhibits the highest modulus, with its magnitude approaching twice that of the (0 1 0) plane. This is because the indenter axis (down a^*) for the (1 0 0) measurements is approximately parallel to the 2D layers, indicating that the phosphonoacetate ligands are stiff and able to withstand certain extent of elastic strains (such as translational and torsional motions of polyhedra, bond stretching and bending, or combinations of the above). As depicted in Fig. 1i, when indenting the (0 0 1) face, the layers are effectively inclined at an oblique angle to the indenter axis, explaining why the modulus of

(0 0 1) was found to lie between those of the (1 0 0) and (0 1 0) planes. Based on the crystal structure, it is anticipated that indenting along the c -axis would confer the largest stiffness as the indenter axis will be aligned approximately parallel to the 1-D M–O–M (Cu–O–Cu) chains.

3.2.2. Hardness anisotropy

It is noted that the hardness of a material is not a unique property but is a function of the test method, the chosen test parameters (e.g. indenter tip geometry, applied load, indentation depth) and the model adopted to calculate the hardness values. Therefore the hardness measurements of single crystals obtained by different test methods are often not directly comparable, unless the main features of the tests are similar. Fig. 4 shows the hardnesses of polymorphs 1 and 2, measured on different crystal facets with a Berkovich nanoindenter, under the dynamic CSM ($h_{\max} < 500$ nm) and quasi-static ($h_{\max} \approx 490$ nm) modes – both appeared to exhibit a similar trend. The hardness data presented in this section were analysed using the O&P method (Eqs. (3) and (4)), in which the anisotropy and pile-up effects are not accounted for.

The degree of hardness (H) anisotropy of polymorph 1 was found to be small, with $H_1(1\ 0\ 0):(0\ 1\ 0):(0\ 0\ 1):(0\ 1\ 1) = 1.05:1.11:1.06:1.00$. The (1 0 0) and (0 0 1) planes are harder than (0 1 1) by only ~ 5 –6%, while the (0 1 0)-oriented face is the hardest among the four indented facets, with a maximum change in hardness of $\sim 11\%$. Polymorph 2 also demonstrates a similar level of anisotropy with $H_2(1\ 0\ 0):(0\ 1\ 0):(0\ 0\ 1) = 1.00:1.12:1.04$, with the

(0 1 0)-oriented facet being the hardest. Here, it is interesting to note that, regardless of its lamellar structure, the maximum change in hardness is only $\sim 12\%$. However, it can be seen from Table 2 that the average hardness of polymorph 1 (4.2–4.7 GPa) is approximately a factor of two greater than that of polymorph 2 (2.3–2.5 GPa). This suggests that the dimensionality and connectivity of the underlying framework contribute to the hardness of hybrid inorganic–organic materials. Moreover, work on inorganic crystalline solids has found increasing evidence [37–39] that the shear modulus (G) is correlated to the hardness. Since the shear modulus measures the resistance towards shape change and is proportional to the strain energy of a dislocation, the movement of dislocation is impeded in crystals of higher G (and hence its higher hardness), when shear stresses are generated via an indenter. Simply based on the measured hardness of the hybrid crystals, we may deduce that the shear modulus of polymorph 1 will be higher than that of polymorph 2.

Despite the large elastic anisotropy detected in hybrid framework crystals (Section 3.2.1), the hardness measurements exhibit relatively weak dependence on crystallographic orientation. Unlike modulus measurements, which monitor only the elastic unloading response of an indenter, hardness measurements are affected by both elastic and plastic deformation mechanisms. For crystalline solids, the hardness anisotropy is an obvious manifestation of dislocation interactions in the plastic zone, in response to the type of indenter facet geometry used to induce the pressure [40]. Recent studies on single crystals [41,42] have found that complex stress states developed within the small volume located beneath the indenter tip, where multiple slip systems can be active simultaneously to accommodate plastic flow. For high-symmetry cubic crystals, it has been suggested [14] that the small hardness anisotropy is caused by identical slip systems that are operational (and hence the averaging of intrinsic hardness values) when indenting differently oriented crystal faces. Conversely, the current polymorphs exhibit small hardness anisotropy despite having low-symmetry crystals with a limited number of active slip systems. Only one possible slip system is available in monoclinic (polymorph 1: $\langle 0\ 0\ 1 \rangle \{1\ 0\ 0\}$) and in triclinic (polymorph 2: $\langle 0\ 0\ 1 \rangle \{0\ 1\ 0\}$) crystal systems [43]. Further investigations will be needed using transmission electron microscopy (TEM) techniques to gain insights into the plastic deformation mechanisms of crystalline hybrid frameworks. Previous TEM studies on nanoindented inorganic crystals [44] have found twinning deformation to be operational at ambient conditions, but a dislocation glide mechanism predominates at elevated temperatures.

A closer examination of the P – h curves of polymorphs 1 and 2 (Fig. 2) reveals two interesting features. First, although all indents were made to the same maximum depths ($h_{\max}$), the relative hardness of the different crystal facets cannot be rationalized simply by comparing the magnitude of their loads. This is true especially when the O&P method is employed to analyse planes with different

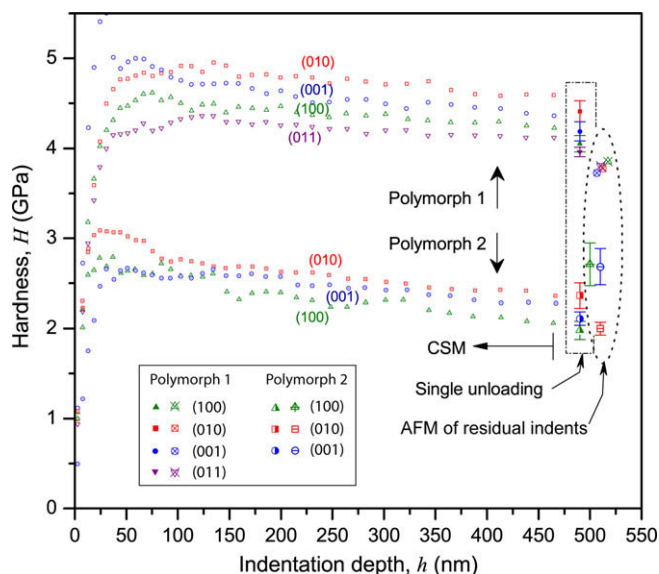


Fig. 4. Indentation hardness of polymorphs 1 and 2 as a function of crystallographic orientation and test method. Error bars for the CSM data are omitted for clarity but their values can be found in Table 2. Hardness data from single unloading experiments are plotted at ~ 490 nm. The pile-up-corrected hardness values determined from AFM data are plotted at depths of just over ~ 500 nm.

contact stiffness (S). The reason partly lies in the use of Eq. (4), where the extent of elastic recovery, $h_e = 0.75(P/S)$, is clearly dependent upon both P and S . Secondly, particularly for the case of polymorph 2, bursts of displacements or “pop-in” events can be detected on all indented crystal facets. This phenomenon originates from the breakage of the (weaker) hydrogen bonds responsible for binding the 2D layers together. It can be seen that staircase-like pop-ins are more prominent on the (0 0 1) face, reflective of the sequential slip mechanism associated with shearing of the oblique layers (Fig. 1i). In contrast, huge displacement bursts (up to ~ 50 nm) occurred on the (1 0 0) face, when the layers are oriented approximately parallel to the indenter axis (Fig. 1g). The combination of pop-ins and radial cracking resulted in the decline of hardness as the indentation depth increases, which also gave rise to bigger experimental scatter.

3.2.3. Pile-up corrected modulus and hardness

The results presented so far have been analysed using the O&P method [24], which is formulated based on elastic contact mechanics. One of its limitations lies in the precise determination of the contact area (A_c) when there is extensive pile-up around the indentation. For isotropic materials, pile-up can result in the underestimation of A_c and therefore the modulus and hardness become overestimated [13,45]. For anisotropic systems, however, its effects on modulus and hardness anisotropy are difficult to predict. Here, a second approach is being attempted to measure the degree of anisotropy, by establishing A_c directly from the 3D geometry of residual indents (at fully unloaded state) obtained from the AFM. The contact boundary is assumed to coincide with the peak point in the pile-up zone, and the (residual) contact area was calculated by integrating the area lying within the boundary [46].

The AFM topographic images of the four low index faces of polymorph 1 and their corresponding cross-sectional profiles are presented in Fig. 5. In all cases, although the maximum penetration depths were the same ($h_{\max} = 500$ nm), their residual depths demonstrate different levels of elastic recovery. The shape of the profiles and the amount of material upheaval are strongly dependent upon the crystallographic orientation. On the (1 0 0)- and (0 1 1)-oriented faces, it can be seen that pile-ups occur only ahead of the sides of the Berkovich tip. Conversely, on the (0 1 0)- and (0 0 1)-oriented faces, similar extents of material upheaval were detected ahead of the corners and on the sides of the tip. Figs. 3a and 4 show that the data points of M and H calculated from residual indents are relatively lower because of pile-ups, although the current analysis does not account for area change due to elastic recovery. The pile-up corrected modulus (denoted by the subscript c) was found to be M_{1c} (1 0 0):(0 1 0):(0 0 1):(0 1 1) = 1.91:1.10:1.00:1.21, which is comparable with that obtained using the O&P method. The corrected hardness, however, exhibits a lower degree of hardness anisotropy, with H_{1c} (1 0 0):(0 1 0):(0 0 1):(0 1 1) = 1.03:

1.01:1.00:1.02. The maximum change in hardness determined by this approach is only $\sim 3\%$, as opposed to $\sim 11\%$ given by the O&P method.

The topography and cross-sectional profiles of polymorph 2 are depicted in Fig. 6. In comparison with the (1 0 0)- and (0 0 1)-oriented faces, the amount of pile-up observed in the (0 1 0) face is more significant (over 250 nm above the original surface, see Fig. 6e). It can be seen that the pile-up behaviour is highly anisotropic (Fig. 6a–c), indicative of the underlying 2D layered structures (Fig. 1g–i). From Figs. 3b and 4, it is interesting to note that the pile-up corrected modulus and hardness of the (1 0 0) and (0 0 1) faces are relatively higher compared with the O&P method, but are relatively lower for the (0 1 0) face. By accounting for pile-up effects (but disregarding elastic recovery), the degree of anisotropy for the corrected modulus and hardness were found to be M_{2c} (1 0 0):(0 1 0):(0 0 1) = 2.24:1.00:1.88 and H_{2c} (1 0 0):(0 1 0):(0 0 1) = 1.36:1.00:1.34, respectively. Therefore, a considerably larger degree of anisotropy was detected in both cases, especially in the case of hardness. Also, in comparison with the O&P outcome, the order of hardness has changed completely to $H_{(100)} > H_{(001)} > H_{(010)}$, which is in good correlation with the modulus: $M_{(100)} > M_{(001)} > M_{(010)}$.

3.2.4. Onset of plasticity and stress–strain response by spherical indentation

The elastic–plastic transition cannot be easily studied using a sharp (Berkovich) indenter due to the highly localized deformation induced beneath the pointed tip, but a spherical tip offers a larger surface contact area at small penetration depths, therefore delaying the onset of plasticity. Moreover, by exploiting its capability to generate changing contact strain as a function of indentation depth, the elastic limit (yield pressure) can be estimated and the indentation stress–strain curves of different crystal facets can be extracted.

Fig. 7a shows the typical P – h curves of polymorph 2 obtained with a spherical indenter ($R = 10$ μm). In comparison with typical curves from a sharp indenter (Fig. 2b), it is evident that all crystal faces responded differently towards the strain field generated by a spherical tip. It can be seen that the magnitude and frequency of pop-ins have changed significantly. The (1 0 0)- and (0 0 1)-oriented faces, in particular, sustained $\sim 60\%$ less surface penetration at the corresponding load levels. Their mechanical responses are similar since the difference in terms of the orientation of the layers (Fig. 1g and i) would be indistinguishable under a (large) spherical contact. A unique feature of the (0 1 0)-oriented plane concerns its time-dependent creep deformation within the hold segment ($\alpha \rightarrow \beta$ in Fig. 7b). It should be emphasized that such a response cannot be detected under a sharp indenter (see Fig. 2b for comparison). The effect of time-dependent plasticity can best be examined in a displacement–time (h – t) plot, as shown in Fig. 7b. For the chosen test conditions, the displacement rate (dh/dt) of the (0 1 0) face at the max-

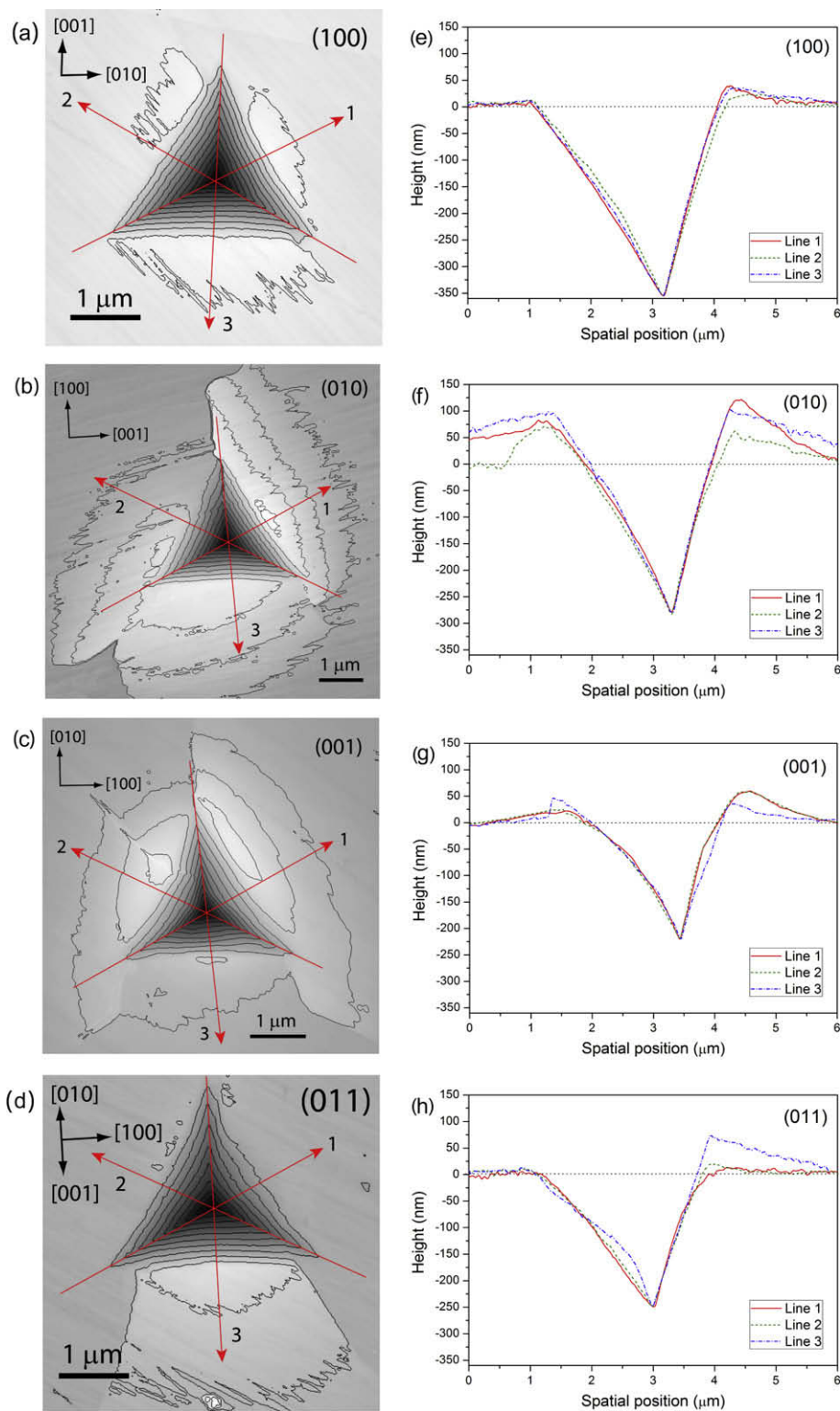


Fig. 5. (a–d) The typical AFM height topology obtained from the (residual) Berkovich indents of polymorph 1, corresponding to the P – h curves depicted in Fig. 2(a). Their cross-sectional profiles along the three designated directions are plotted in (e–h).

imum load was found to be $\sim 8.6 \text{ nm s}^{-1}$, almost two orders of magnitude higher than those measured for the (0 0 1) and (1 0 0) planes ($\sim 0.1 \text{ nm s}^{-1}$). In this case, the strongly anisotropic creep behaviour is clearly attributable to the directionality of inter-layer hydrogen bonding.

The P – h curves of polymorph 2 exhibit distinct pop-in phenomena (Fig. 7a) which are commonly associated with the nucleation of mobile dislocations that are linked to the onset of plasticity [21]. Therefore, it would be interesting to estimate the critical resolved shear stress (τ_{crit}) of different

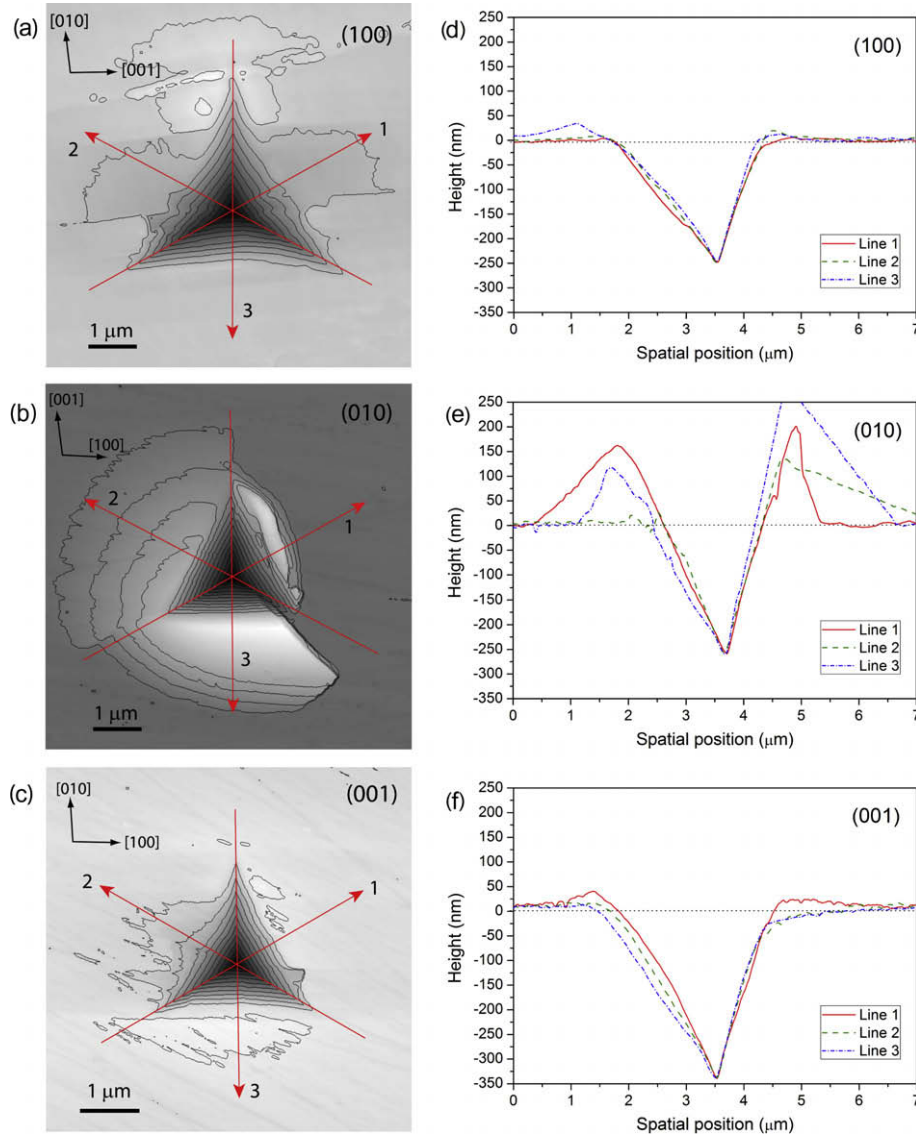


Fig. 6. Typical AFM topography and cross-sectional profiles of polymorph 2 along its three main crystallographic orientations.

oriented planes at the onset of plasticity by Hertzian elastic contact theory. Doing this requires knowledge of the load corresponding to the first pop-in event (P^*) and the reduced modulus of the system (E_r found from Eq. (7)), as given by [47]:

$$\tau_{crit} = 0.31 \left(\frac{6P^* E_r^2}{\pi^3 R^2} \right)^{\frac{1}{3}} \quad (5)$$

τ_{crit} is found directly below the centre of the indenter, at a distance of about half the contact radius ($\sim 0.5a$), and acts on planes that are inclined at 45° to the surface. It can be seen from Table 3 that the depths at which the first pop-in was detected in the (100)- and (001)-oriented faces were similar ($h^* \approx 130$ nm) and so were their pop-in loads ($P^* \approx 7$ mN). When the indenter axis is aligned approximately parallel to the hydrogen bonded layers (i.e. along the a^* - and c^* -directions in Fig. 1g and i), their theoretical shear strengths were found to be equivalent in

both directions (within experimental error): $\tau_{crit} = 0.98$ – 1.11 GPa. However, when the indenter axis was oriented approximately perpendicular to the layers (i.e. along the b^* -direction in Fig. 1h), the first pop-in was delayed until $h^* \approx 300$ nm, and a relatively lower value was found: $\tau_{crit} \approx 0.76$ GPa. Since the theoretical shear strength of a crystalline material is of the order of $G/10$ (e.g. [48]), it is estimated that the shear modulus (G) of polymorph 2 will be at least 7–11 GPa, with higher moduli expected in directions parallel to the 2D layers. Fig. 8 depicts the typical AFM topography and 2D profiles of a spherical indent, obtained at a maximum load of 50 mN on the (100)-oriented facet. It can be seen that the plastic deformation mechanism is characterized by the formation of slip steps (bands) inside the indent and in its vicinity. The height of the slip steps can range from ~ 10 to 50 nm, which is consistent with the size of pop-ins detected in the P – h curves (Fig. 7a). Here, the fact that all steps are oriented along

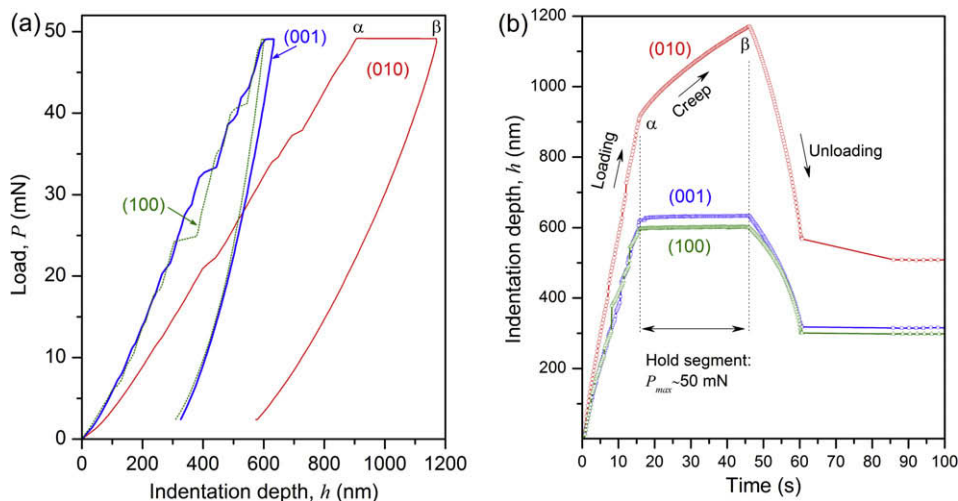


Fig. 7. (a) Typical P – h curves of the crystal faces of polymorph 2 obtained with a spherical nanoindenter. The maximum loads were 50 mN, with a hold time of 30 s prior to unloading. (b) The indentation depth vs. time curves that correspond to the data presented in (a), in which extensive creep deformation is indicated by the segment $\alpha \rightarrow \beta$, found on the (0 1 0) facet.

$\langle 0\ 0\ 1 \rangle$ reveals their formation to be associated with the breakage of inter-layer hydrogen bonds. Similar deformation pattern was found on the (0 0 1)-oriented facet with parallel steps running along the $\langle 1\ 0\ 0 \rangle$ direction (figure not shown here).

The elastic–plastic information contained within the P – h curves of spherical indentation can be better represented in the form of “indentation stress–strain” curves. The indentation stress (P_m) is effectively the mean contact pressure (i.e. hardness) under the spherical tip [49]:

$$P_m = \frac{P}{\pi a^2} \quad (6)$$

The relationship between contact radius (a) and contact depth (h_c) is given by $a = \sqrt{2Rh_c - h_c^2}$ (assuming no pile-up) [50]. In the elastic regime, P_m is linearly proportional to the indentation strain (a/R), as given by the Hertzian relationship [47]:

$$P_m = \frac{4E_r}{3\pi} \left(\frac{a}{R} \right) \quad (7)$$

Fig. 9 shows the typical indentation stress–strain curves of polymorphs 1 and 2. It can be seen that, at lower strain levels ($a/R < \sim 0.1$), the crystal faces deform elastically since a linear Hertzian relationship defined by Eq. (7) can be used to relate stress and strain. Each straight line indicates the expected stress–strain relationship for purely elastic loading (before any pile-up occurs), with a gradient of $4E_r/3\pi$. The yield pressure (P_y) denotes the critical stress corresponding to elastic–plastic transition, and its values for differently oriented planes are summarized in Table 3. We note that all crystal faces in polymorph 1 have higher yield pressures ($P_y \approx 1.8$ – 2.3 GPa), and in the plastic regime they demonstrate strain-hardening characteristics resembling that of power-law hardening. The strain-hardening character of each plane is also unique to the specific

crystallographic orientation. At larger strains, the yield pressure of the indented planes can be ranked in the order $P_y(0\ 1\ 0) > (0\ 0\ 1) > (1\ 0\ 0) > (0\ 1\ 1)$, which is in good agreement with the hardness ranking obtained from the O&P method (see Fig. 4, within experimental scatter). This finding is consistent with previous studies that show hardness to be directly proportional to the yield pressure, i.e. $H = C \cdot P_y$ [51], where C is the constraint factor (i.e. ratio of hardness to yield pressure). In polymorph 1, which has a 3D hybrid framework, it was found that $C \sim 2$ – 2.4 .

By contrast, all crystal faces on polymorph 2 exhibit relatively low yield pressures ($P_y \approx 0.7$ – 1.9 GPa), which translate into lower hardnesses. Their constraint factors are lower along the directions of the 2D layers ($C \sim 1.2$ – 1.5), while in the normal direction, i.e. the (0 1 0) face, it is higher by a factor of two ($C \sim 3.6$) due to the lower P_y . In comparison with conventional materials, we note that a C -value of ~ 1.5 is commonly associated with ceramic and glasses (materials with low ratio of elastic modulus to yield pressure), whereas a C value of ~ 3 is typical of metallic materials [52]. On the (0 0 1) and (1 0 0) planes, abrupt drops in stresses due to pop-in phenomena appear to affect their strain-hardening behaviour. However, if pop-ins are to be disregarded, their stress–strain curves resemble that of an elastic–perfectly plastic solid. Our findings suggest that the availability of 3D connectivity (or higher dimensionality) in hybrid materials (polymorph 1) can induce more dislocation interactions within the crystal-line structure, leading to a greater strain-hardening response. However, further investigation by TEM is warranted to elucidate the mechanisms of plasticity under the indents of hybrid materials with different dimensionalities.

3.2.5. Fracture toughness anisotropy

Finally, we attempt to measure the resistance against crack propagation in copper phosphonoacetate hybrid

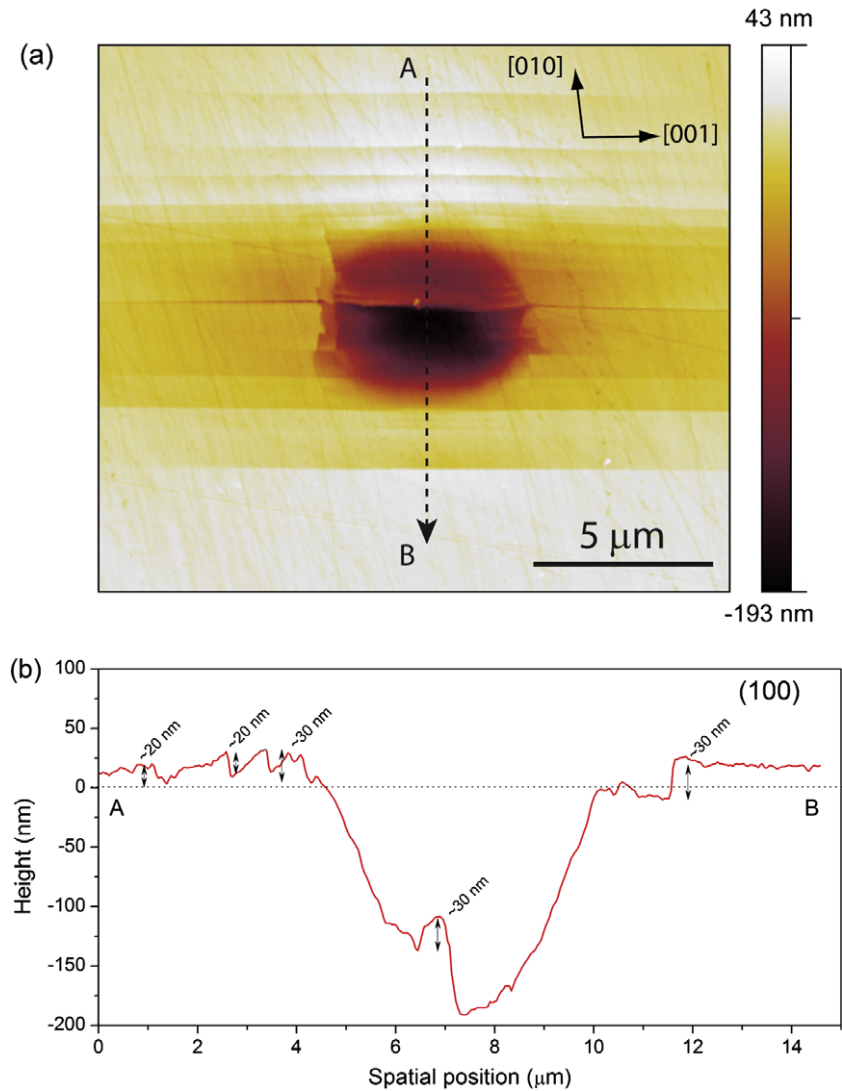


Fig. 8. (a) The typical AFM topography and (b) 2D cross-sectional profile of a residual spherical indent, obtained at a maximum load of 50 mN on the (1 0 0)-oriented facet. The slip steps inside and around the vicinity of the indent can be clearly detected.

frameworks. The fracture toughness (K_c) of different crystal facets was estimated by means of radial cracks emanating from the Berkovich indents under applied loads of 50–100 mN. The expression of Laugier [53,54] was used to estimate K_c from the radial crack configurations:

$$K_c = x_v \left(\frac{a_h}{l} \right)^{1/2} \left(\frac{E_s}{H} \right)^{2/3} \left(\frac{P}{c^{3/2}} \right) \quad (8)$$

where $x_v = 0.016$ for a Berkovich tip [55], a_h is the half-diagonal length, l is the crack length and $c = a_h + l$ (see Fig. 10a). It is noted that the original expression by Lawn et al. [56] is not applied here since it is only appropriate for median-radial cracking (produced by a Vickers indenter) and tends to overestimate the fracture toughness in systems that develop only radial cracks. For first-order estimates, the Young's modulus of the sample (E_s) can be approximated from the plane-strain modulus: $M \approx \frac{E_s}{(1-\nu_s^2)}$ [25], and by assuming $\nu_s \sim 0.2$. In fact, due to the experimental

uncertainty, the difference between E_s or M in Eq. (8) can generally be neglected. It was found that K_c is insensitive to the small load range applied here, but is highly dependent upon the crystallographic orientation.

Table 2 shows that the K_c of polymorph 1 ranges from ~ 0.10 to $0.33 \text{ MPa m}^{1/2}$, whereas in polymorph 2 it ranges from ~ 0.08 to $0.12 \text{ MPa m}^{1/2}$. Polymorph 1 therefore exhibits higher toughness values, and may exceed that of polymorph 2 by as much as a factor of four in certain orientations. Our results reveal that reducing the connectivity and/or dimensionality of a hybrid framework can adversely affect its resistance to cracking. The fracture toughness anisotropy in polymorph 1 was found to be $K_{c1} (1\ 0\ 0):(0\ 1\ 0):(0\ 0\ 1) = 2.36:1.00:1.25:1.54$; this is relatively lower in polymorph 2, for which $K_{c2} (1\ 0\ 0):(0\ 1\ 0):(0\ 0\ 1) = 1.00:1.04:1.06$. The observed anisotropy in toughness is also indicative of the anisotropy in surface fracture energy of the different crystal facets [57].

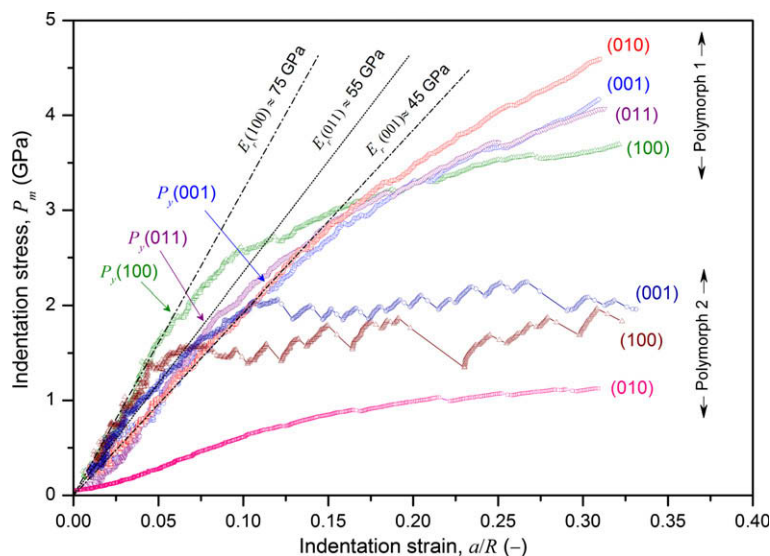


Fig. 9. Indentation stress–strain curves of polymorphs 1 and 2, derived from the spherical nanoindentation data. The transition from purely elastic to plastic deformation is designated by the yield pressure P_y , illustrated here for the (1 0 0), (0 1 1) and (0 0 1) planes of polymorph 1. The straight lines correspond to purely elastic Hertzian contact for estimating the reduced modulus, E_r . In polymorph 2, the abrupt drops in stresses observed in the (0 0 1)- and (1 0 0)-oriented planes are caused by pop-in events.

Table 3

Incipient plasticity information measured along the main crystallographic orientations with a spherical nanoindenter ($R = 10 \mu\text{m}$).

Mechanical properties	Polymorph 1				Polymorph 2		
	(1 0 0)	(0 1 0)	(0 0 1)	(0 1 1)	(1 0 0)	(0 1 0)	(0 0 1)
Yield pressure, P_y (GPa)	~1.9	~2.3	~2.2	~1.8	~1.5	~0.7	~1.9
Constraint factor, C (–)	~2.4	~2.0	~2.0	~2.3	~1.5	~3.6	~1.2
Penetration depth at first pop-in, h^* (nm)	NA				128 ± 10	293 ± 68	127 ± 17
Load at first pop-in, P^* (mN)	NA				6.7 ± 0.4	13.0 ± 2.8	7.7 ± 1.6
Critical resolved shear stress, τ_{crit} (GPa)	NA				1.06 ± 0.06	0.76 ± 0.08	1.05 ± 0.07

The load and penetration depth at the first pop-in were found from P – h curves similar to the ones depicted in Fig. 2b. The yield pressure is determined from the indentation stress–strain curves (Fig. 9).

It is possible to establish relationships between the sub-surface fracture morphology of polymorph 1 and its crystalline structure. On the (1 0 0) plane, four radial cracks can be seen propagating in the $\langle 0 \bar{1} 1 \rangle$ directions, regardless of the indenter geometry (Fig. 10a and b). These cracks, therefore, have to be crystallographically oriented. We established from Fig. 1b that these are the (0 1 1) and (0 $\bar{1}$ 1) planes, and the cracks most likely initiated from the rupture of adjacent carboxylate headgroups linking the quasi-inorganic chains. On the (0 0 1)- and (0 1 0)-oriented faces, both radial and lateral cracks developed accompanied by crack deflections and bifurcations, as depicted in Fig. 10c and d. However, it is noted that cracking is more prevalent on the (0 1 0) faces. Their crystal structures viewed along the indenter axis (Fig. 1c and e) indicate that the phosphonoacetate ligands may have a greater tendency to rupture in the latter case.

Turning to polymorph 2, Fig. 10e depicts an interesting crack pattern that developed on the (0 1 0) plane, indicative of its underlying layered structure which deforms by creep deformation under compressive stresses (see Fig. 7b). By

contrast, (0 0 1)- and (1 0 0)-oriented faces (Fig. 10f and g) exhibit horizontal cracks propagating parallel to the planar axis of the layers (Fig. 1i and g), but with no cracks developed in the transverse directions. We recall that slip steps also formed in conjunction with the cracks; these are visible from the AFM scans (e.g. Fig. 8). Evidently, they originated mainly from the rupture of inter-layer hydrogen bonds and the $\{0 \bar{1} 0\}$ planes are bound to be the cleavage planes. In comparison with (0 0 1), we note that the layers in (1 0 0) are oriented almost parallel to the indenter axis, hence more extensive cracking takes place. Moreover, it can be seen that the residual of the spherical indent on (1 0 0) is clearly asymmetrical (Fig. 10g), bottom pane), reflective of the anisotropic plastic strain field that has developed underneath.

4. Concluding remarks

We have demonstrated the capabilities (along with limitations) of the nanoindentation technique for measuring the anisotropy in the mechanical properties of hybrid inor-

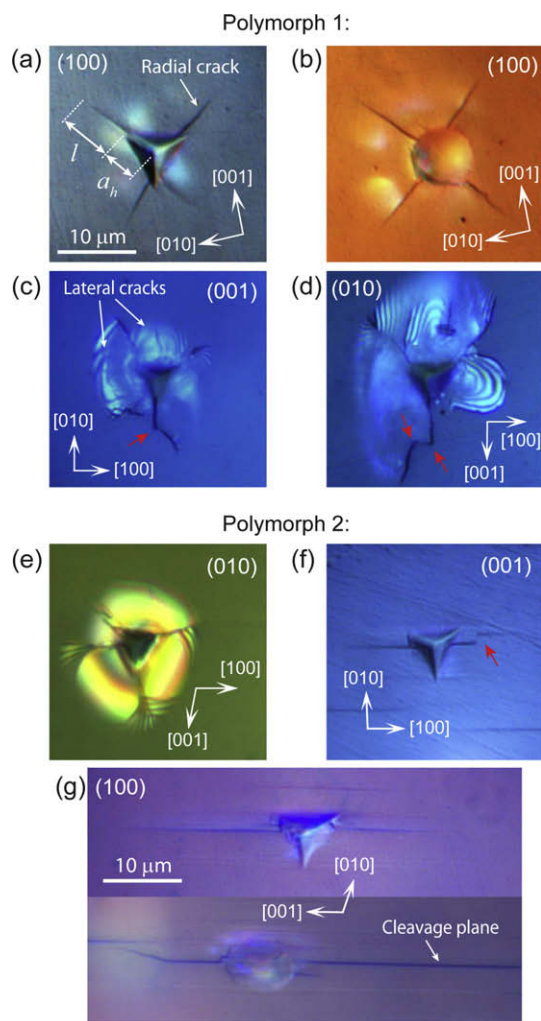


Fig. 10. Interference contrast optical micrographs showing fracture morphology on the main crystal facets of (a–d) polymorph 1 and (e–g) polymorph 2. A combination of radial and/or lateral cracks can be observed, while closely spaced fringes indicate a steeper inclination. All micrographs have the same magnification.

ganic–organic framework materials. The elastic anisotropy of the polymorphic hybrid frameworks was found to be large compared with their plastic anisotropy. The degree of anisotropy along the main crystallographic orientations can be directly correlated to the underlying crystalline structures and their dimensionalities. We have established that the presence of strong covalent bonding coupled with weaker intermolecular bonding (e.g. hydrogen bonds) within the same hybrid framework can give rise to highly directional mechanical responses.

To put our findings in a bigger perspective, the current elastic modulus and hardness data were incorporated into a materials selection map (Fig. 11). In comparison with other common engineering materials, it can be seen that the mechanical properties of the polymorphs are to some extent intermediate between those of purely organic (e.g. polymers) and non-metallic inorganic (e.g. ceramics) solids. However, they populate a region of the chart that is not

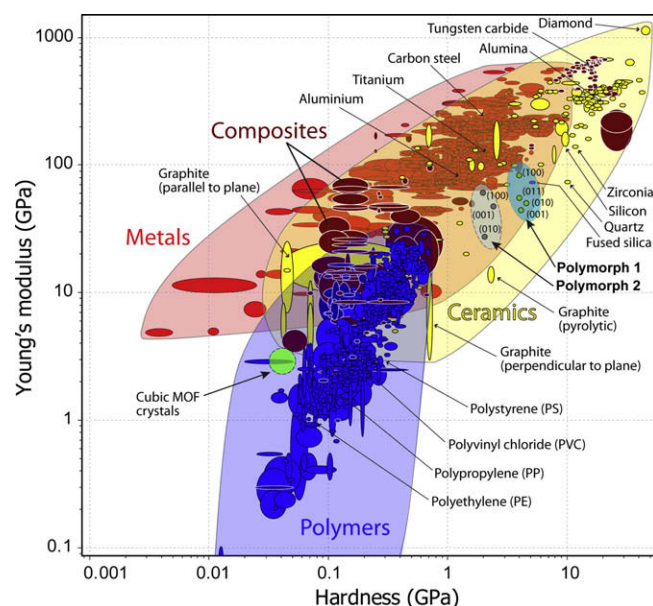


Fig. 11. Young's modulus vs. hardness materials selection map. The elastic moduli and hardnesses of different crystal faces of polymorphs 1 and 2 are presented alongside other common non-metallic inorganic (ceramics) and organic (polymers) materials [59]. The mechanical properties of nanoporous cubic zinc carboxylate (IRMOF-1 or MOF-5) crystals [10] are also plotted. Note that the Young's modulus of each crystal face of polymorphs 1 and 2 was estimated from its indentation modulus via $E_s \approx M(1 - \nu_s^2)$ [14] and by assuming $\nu_s \sim 0.2$. The hardness data obtained from the literature [59] were converted from the Vickers hardness (HVN) values, by assuming $H(\text{GPa}) = 0.010793 \times \text{HVN}(\text{kg mm}^{-2})$.

well represented by other conventional materials. Moreover, it is also interesting to note that the mechanical properties of dense hybrids can be several orders of magnitude greater than those of a nanoporous hybrid framework (e.g. MOF-5 [10]).

The fundamental concepts discovered here are applicable to a broad class of hybrid framework materials with different dimensionalities and are relevant to the eventual use of such materials in a wide range of applications. Due to the enormous diversity of chemical and structural variations that can be envisaged for hybrid frameworks [1], there is arguably an unlimited scope for tuning their mechanical properties to match specific applications. This is essential for a wide range of advanced functional devices, such as thin films, that must satisfy many stringent mechanical requirements before viable applications can be made possible.

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