Structural behaviour of metal-organic framework UiO-66 under extreme pressures

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Metal-organic frameworks (MOFs) are formed of inorganic, metal ion-based nodes connected by organic molecules in an extended configuration. This ‘building block’ structure allows the framework’s chemical or mechanical properties to be tuned for a specific function through replacement or modification of the node and linker[1]. Recently, research has focused on the mechanical properties of MOFs, either to reinforce the crystalline structure under industrial processing conditions or introduce a controlled loss of crystallinity for applications such as drug delivery[2]. The process of amorphization under pressure must be understood for either scenario and as such in situ high pressure studies using multiple techniques are required.

UiO-66 is a zirconium-based MOF with a predicted high stability under pressure. This results from a comparatively stable fcu topology and a large shear modulus due to its highly connected Zr6O8 nodes[3,4]. However, previous research on the family of MOFs with this node has only been carried out to a maximum of 5 GPa, never reaching a fully amorphous phase[5]. Here, multiple in situ techniques were combined to give a detailed view of the structure as it underwent compression. Loss of crystallinity was seen as partially reversible at low pressures, although a structural change occurred at 13 GPa that prevented this recovery if the sample was taken above it. Bonding and coordination around the node were probed through spectroscopic methods to further investigate this structural change. Some crystallinity was unexpectedly observed to survive pressures of 28 GPa, as seen by comparison of X-ray diffraction data to that of mechanically amorphized UiO-66.

This work highlights the need for experimental research on the mechanical properties of MOFs for future industrial processing and demonstrates the behaviour of a prototypical framework under pressures much more extreme than are usually investigated.

References:

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