Thermo-mechanical Properties of Zeolitic Imidazolate Frameworks (ZIFs)

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This thesis uses multiple physical crystallographic techniques to investigate the properties of a specific family of hybrid porous materials, called Zeolitic Imidazolate Frameworks (ZIFs), which are structurally similar to inorganic zeolites.

In one aspect of my research, high-pressure single crystal and powder X-ray diffraction studies were performed on 6 different crystalline ZIFs, finding several phase transitions to previously unknown structures. Importantly, investigations revealed reversible pressure-induced amorphization in one framework, whilst high pressures were also found to affect complete pore evacuation without structural collapse. Bulk moduli were calculated for the materials using the high-pressure data.

The thermal expansion behaviour of ZIFs was initially followed using variable temperature PXRD, which revealed several instances of non-linear negative thermal expansion. However, an irreversible crystalline-amorphous-crystalline transition was observed in one particular framework, which led to an *in-situ* Total Scattering experiment at the ISIS neutron facility. An X-ray total-scattering experiment was performed at the same time. Reverse Monte-Carlo modeling was used to demonstrate the amorphous framework possessed a continuous random network topology similar to that of amorphous silica. The transition sequence was also followed by electron diffraction and nano-indentation studies, which perfectly complimented the Total Scattering studies.

Further X-ray Total Scattering experiments revealed structural isomers of the framework to undergo an identical transition upon heating, regardless of starting network topology. X-ray Total Scattering and subsequent PDF analysis was also used to confirm that mechano-chemical ball-milling of the materials produced an identical amorphous network topology.

Curiously, ball-milling also facilitated the amorphization of ZIFs with different chemical compositions, though these materials were found to be resistant to thermal amorphization. Further X-ray Total Scattering studies are currently ongoing to determine the identity of these amorphous networks.

The amorphization process discovered in this thesis was used to produce a magnetic amorphous network, whilst it has also shown to be useful in irreversibly trapping I_2 molecules inside ZIFs, through post I_2-uptake amorphization. It has also opened up routes to optically and electronically active glass-like materials.

Overall, the thesis provides not only a stunning example of the use of RMC modeling (on Neutron and X-ray diffraction data) in the first characterization of an amorphous hybrid framework, but also encompasses crystallography under extreme conditions, structure property relationships, electron diffraction and other techniques complimentary to crystallographic methods. The ZIFs provide a perfect example of a framework family with which to link every single major aspect of physical crystallography, whilst also opening up an entirely new field of amorphous hybrid frameworks for discussion.

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