MS21-O5 Development of a moderate pressure cell for the small molecule beamline I19 at Diamond Light Source

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Since the invention of diamond anvil cells (DACs), they have become the primary pressure cell design that has dominated high pressure science when kbar pressures are required. They have made data collection (both single-crystal and powder) routine, however they are not without their limitations. Fine control of pressure is difficult to achieve and measure accurately, particularly at lower pressures. For most molecular systems studied at pressure, this is not an issue, though often interesting phase behaviour or compressibility can occur even below 1 kbar. Currently there is relative paucity of pressure cell designs with cells capable of generating pressure from ambient pressure to several kbar.

Currently, gas cells have been made which allow 100's of bar of pressure to be applied to a crystal using a compressed gas, though these systems have primarily been built to study the uptake of gases into porous materials [1] or chemical reactions between the gas and the solid sample at elevated temperature and pressure.[2-4] This falls someway short of the kbars of pressure required to close the gap on DACs.

Here we have begun to develop a static liquid cell capable of reaching 4 kbar that would not only close the pressure gap between current gas cell technology and DACs, but allow the investigation of materials from vacuum, to 4 kbar with the sample in a hydrostatic environment and as a function of very small pressure steps (ca 1 bar), allowing for the first time a high degree of crystallographic detail to be obtained without the usual limitations associated with modern DAC technology. This will allow us to observe structural changes, phase transitions and calculate with much greater precision the bulk moduli of soft molecular materials.

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Keywords: moderate pressure crystallography, new instrumentation

MS22. High response systems in practical and extreme conditions

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MS22-O1 Time-resolved X-ray diffraction reveals the origins of high dielectric and electromechanical responses in ferroelectrics

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Ferroelectrics are the class of materials in which two or more equivalent states of spontaneous polarization are switchable by an external electric field. Ferroelectrics are interesting for their excellent dielectric and piezoelectric properties. Although the strong responses of ferroelectrics to an external electric field are clearly connected to the intense dynamics of a ferroelectric switching, the details of the accompanying processes remain unclear. For example, it is particularly difficult to separate intrinsic (atomic) and extrinsic (domain-wall motion) contributions. Both of them may be equally important for the materials properties, they could be activated by electric fields of different magnitudes and have different temporal dynamics.

This presentation explores the mechanisms of high dielectric and piezoelectric response in ferroelectrics and related (e.g. relaxor ferroelectric) systems using time-resolved X-ray diffraction [1]. We benefit from the capabilities of X-ray diffraction to sense the variation of atomic, mesoscopic, macroscopic and even disorder parameters at the same time. This way the dynamics of e.g. atomic positions, domain sizes and lattice parameters under electric field can be investigated and interconnected with one another. We will demonstrate how our recent X-ray diffraction studies of $Sr_{0.5}Ba_{0.5}Nb_2O_6$ single crystals revealed that electromechanical response of uniaxial ferroelectrics may express the correlation between the lattice parameter(s) and their domain size(s) [2]. We will further show how an anomalous X-ray scattering allows studying intrinsic dynamics of polarization reversal in the perovskite-based $BaTiO_3$-$BiZn_{0.5}Ti_{0.5}O_3$.

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MS22-O2 Structural flexibility in prototypical zeolitic imidazolate frameworks

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In recent years, it has become apparent that certain Metal-Organic Framework (MOF) compounds demonstrate remarkable structural flexibility. Understanding this behaviour is crucial to interpreting adsorption in porous compounds. MIL-53 provides the prototypical example, undergoing an anisotropic 'breathing' transition on exchange of adsorbate molecules, by cooling or by application of mechanical pressure.[1] Phase transitions also influence the gas adsorption behaviour of Zeolitic Imidazolate Frameworks (ZIFs), a significant subclass of MOFs. ZIF-8 demonstrates a gate-opening transition on adsorption of gas molecules and application of mechanical pressure,[2,3] which is achieved by a rotation of the methylimidazolate linker units to open the windows of the sodalite cages. ZIF-7, also bearing a sodalite framework, demonstrates a slightly different gate-opening transition, achieved by a concomitant rotation of the benzimidazolate linkers and a distortion of the structure.[4]

We report new results in the understanding of the nature of the phase transitions in ZIF-7 and -8 and most significantly, the first example of extreme isotropic flexibility in ZIF compounds.[5] Desolvated ZIF-4(Zn) undergoes an isotropic phase transition on cooling from 298 K to 80 K, leading to a 23 % reduction in pore volume and a closure of the pore space. This porous to non-porous phase transition was investigated by *in situ* synchrotron powder X-ray diffraction, which allowed the mechanism to be determined and also to confirm its discontinuous nature. The new low temperature structure is marginally less dense than that of the densest known ZIF phase, ZIF-zni. By combining structural results with DSC measurements and DFT calculations, the driving force for this new and unexpected transition was established. Using these results, it is now possible to understand the gas adsorption behaviour of this important framework compound.

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